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Solarization of Glass by Soft X-Rays

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Window glass was solarized (colored brown) with x-rays whose wave-lengths were principally those of the K lines of copper (1.54 and 1.38A). The relative amount of light transmitted by the solarized, with respect to that transmitted by the unsolarized, part of the glass was measured with the aid of a Weston Photronic cell. The effect of x-ray tube current, voltage, time of exposure and the tendency of the solarization to fade with time, at several temperatures, were investigated.

INTRODUCTION

THE coloration of the walls of old x-ray bulbs has been known for years. In 1899 Villard[1] showed that x-rays exert a chemical action not only on the photosensitive salts on a photographic plate but also produce an image in the glass itself. Elster and Geitel,[2] Holzknecht,[3] Goldstein,[4] Dauvillier,[5] Perrine[6] and Bayley[7] have investigated this and related phenomena. The authors became interested in this kind of solarization after observing the ease with which glass cells, used for irradiating biological materials with x-rays, could be solarized.

EXPERIMENTAL

The x-rays were supplied by a gas tube having a copper target. The relative positions of the sample, target and window of the x-ray tube are shown in Fig. 1 (top). The tube was operated on full-wave rectified alternating current. The voltages subsequently mentioned were measured with a spark gap having 20 mm spheres. A photograph taken with an oscillating crystal spectrograph showed that the radiation transmitted through

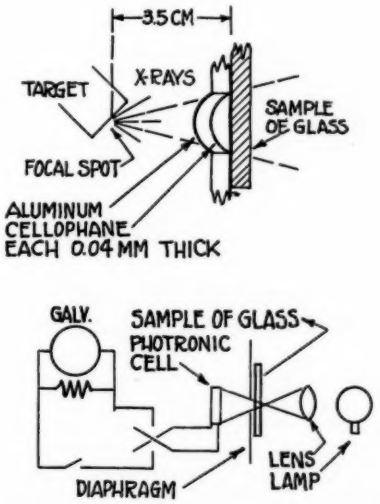

FIG. 1. Top: position of sample with respect to target and window. Bottom: arrangement for measuring percent of light transmitted.

[1] Villard, Comptes Rendus **129**, 882 (1899).
[2] Elster and Geitel, Ann. d. Physik und Chemie **62**, 4, 599–602 (1897).
[3] Holzknecht, Deutsch. Phys. Gesell. Verh. **4**, 2, 25 (1902).
[4] Goldstein, Preuss. Akad. Wiss. Berlin, Sitz. Ber. **10**, 222 (1901).
[5] Dauvillier, Comptes Rendus **171**, 627 (1920).
[6] Perrine, Phys. Rev. **22**, 48 (1923).
[7] Bayley, Phys. Rev. **24**, 495 (1924).

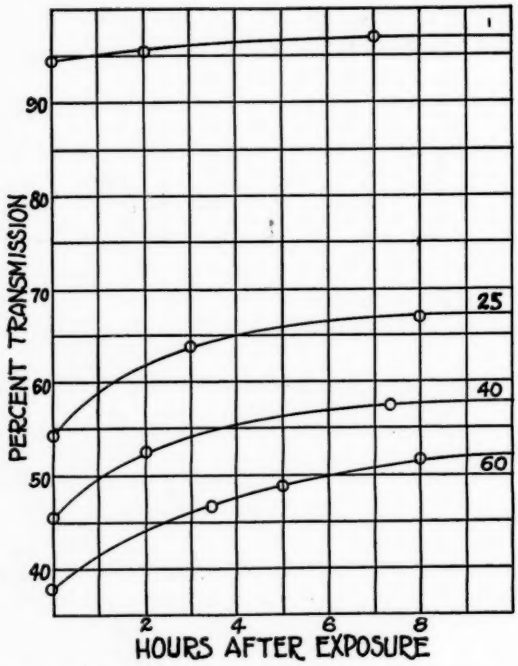

FIG. 2. Variation of transmission with time of recovery for various times of exposure (minutes). Potential difference across x-ray tube, 45 kv; current through the tube, 10 milliamperes. Temperature, 26°C.

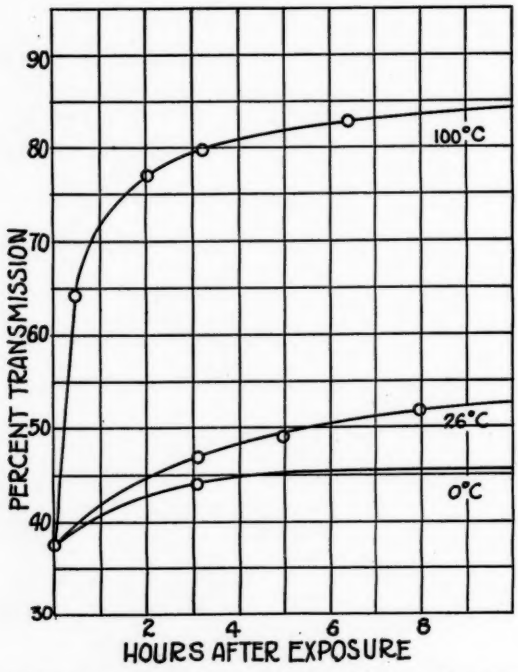

FIG. 3. Variation of transmission with time of recovery for various temperatures during recovery. Normal temperature, 26°C; potential difference across x-ray tube, 45 kv; current through tube, 10 milliamperes; time of exposure, 1 hour.

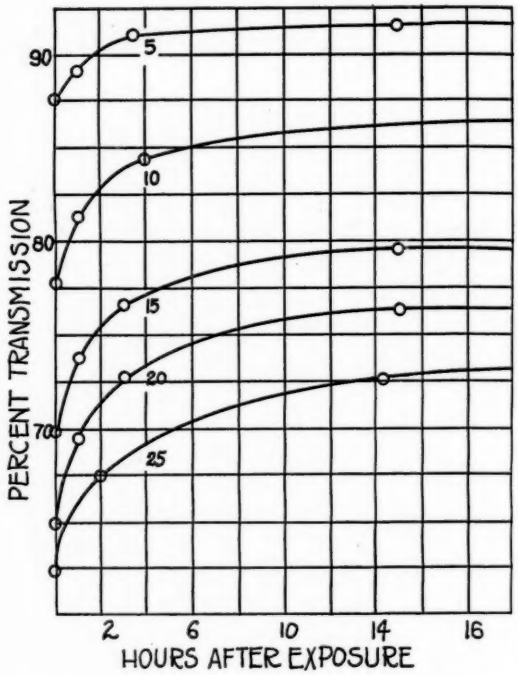

FIG. 4. Variation of transmission with time of recovery for various x-ray tube currents (milliamperes). Potential difference across tube, 30 kv; time of exposure, 15 min.; temperature, 26°C.

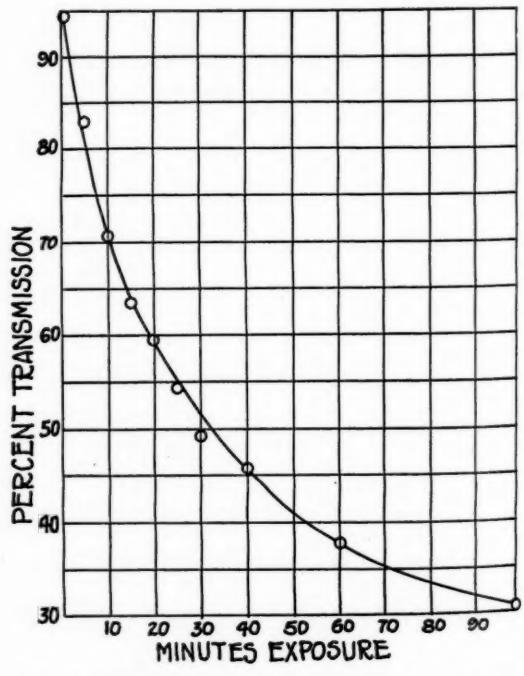

FIG. 5. Variation of initial transmission with time of exposure. Potential difference across the x-ray tube, 45 kv; current through tube, 10 milliamperes; temperature, 26°C.

the window consisted principally of the K lines of copper (1.54 and 1.38A).

The relative amount of light transmitted by the solarized, with respect to the unsolarized, part of the glass was measured with the aid of a Weston photronic cell arranged in a way similar to that described by Storey and Kalichevsky[8] and shown in Fig. 1 (bottom). The percentage of the light transmitted was taken to be $(r/r_0)\times 100$, where r is the mean deflection of the galvanometer to the right and left when the light came through the solarized portion and r_0 that for the unsolarized portion. It was assumed that the error in deflection caused by the change in sensitivity of the cell due to the coloration was small in comparison with the deflection that arose because of the light actually reaching the cell through the glass specimen and spot. The transmission of the clear glass, referred to air, was 91 percent. The current sensitivity of the shunted galvanometer was 41.45 microamperes per cm at a scale distance of 50 cm. The resistance of the circuit external to the cell was about 5.5 ohms. It was inferred that the current was proportional to the intensity of illumination incident on the cell. Readings were reproducible with greater accuracy and convenience than those taken on a spectrophotometer, where the intensity of two fields had to be compared visually. Between readings the samples were kept in subdued incandescent light. The pieces of glass[9] used were all cut from the same plate and were about 0.3 cm thick, 10 cm long, and 2.5 cm wide.

[8] Storey and Kalichevsky, Ind. Eng. Chem., An. Ed., 5, May 15 (1933).

Conclusions

Under all conditions, the recovery of the material from solarization seems to be logarithmic. The rate of increase of transmission after irradiation is increased by (1) reducing the exposure time (Fig. 2), (2) heating the specimen during recovery (Fig. 3) and (3) decreasing the current through the x-ray tube (Fig. 4). The initial transmission, i.e., the transmission immediately after irradiation, increases nearly exponentially as the exposure time decreases (Fig. 5). Preliminary tests with a spectrophotometer showed that, for a sample of glass similarly irradiated, recovery is more rapid for the longer wave-lengths and that the initial transmission is greater also in this case. Typical spectral regions used were 6500, 5500, and 4600A.

[9] Samples of window glass manufactured by the Libbey-Owens-Ford Glass Co.

The Determination of the Structures of Methane Derivatives by the Electron Diffraction Method

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The molecular structures of several bromine and iodine derivatives of methane have been determined by the electron diffraction method. For tertiary butyl bromide it has been found that the tertiary carbon atom has the tetrahedral angles between the valence bonds, and the interatomic distances are: tertiary C− methyl C 1.55A and tertiary C−Br 2.06A. In methyl bromide and iodide the C−X distances are 2.06 and 2.28A, respectively. In methylene bromide and iodide it has been found that the angle between the C−X bonds is 125° and the interatomic distances are: C−Br 2.03, Br−Br 3.61, C−I 2.28 and I−I 4.06A. In bromoform the angles formed by the C−Br bonds are 115°, and the interatomic distances are: C−Br 2.05 and Br−Br 3.46A.

INTRODUCTION

THIS investigation was undertaken to determine the structures of several halogen derivatives of methane and to determine the effect of halogen substitution upon the angles between the bonds of the carbon atom. The theoretically predicted deviations from 109.5°[2] were in agreement with the x-ray diffraction data for methylene chloride and chloroform,[3] although the electron diffraction results for the same compounds[4] showed slightly smaller deviations from 109.5° than x-ray results. It seemed desirable, therefore, to determine the angle between the valence bonds of the carbon atom in bromine and iodine substituted methanes by the electron diffraction method. Tertiary butyl bromide was investigated to study the effect of methyl groups on the tetrahedral angles of a tertiary carbon atom. The tertiary butyl halides have much larger electric moments than the normal butyl and other aliphatic halides;[5] this difference has been explained as an induction effect on the three adjacent methyl groups.[6]

The angular intensity of electrons diffracted by gas molecules with random orientation may be calculated by the equation[7]

$$I = k \sum_i \sum_j \psi_i \psi_j (\sin X_{ij}/X_{ij}) \qquad (1)$$

in which

$$X_{ij} = 4\pi l_{ij} (\sin \theta/2)/\lambda. \qquad (1a)$$

I is the relative intensity of electrons scattered at the angle θ, k is a constant under experimental conditions, the ψ's are the electron scattering coefficients of the atoms, l_{ij} is the distance between the ith and jth atoms of the molecule and λ is the wave-length of the incident electrons. Previous work[8] has shown that Z, the atomic number of the atom, may be substituted for ψ in Eq. (1) rather than the expression derived by Mott.[9] This simplification has been employed in this work.

EXPERIMENTAL PROCEDURE AND RESULTS

The apparatus and procedure was that described in a previous paper.[10] The electron diffraction photographs were obtained with electrons having a velocity corresponding to 45 kv.

[1] National Research Fellow in Chemistry.

[2] J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933).

[3] L. Bewilogua, Phys. Zeits. **32**, 265 (1931); P. Debye, Zeits. f. Elektrochemie **36**, 612 (1930).

[4] R. Wierl, Ann. d. Physik [5] **8**, 521 (1931).

[5] C. P. Smyth, *Dielectric Constant and Molecular Structure, Appendix 1*, New York, The Chemical Catalog Co., Inc. (1931).

[6] C. P. Smyth and R. W. Dornte, J. Am. Chem. Soc. **53**, 543 (1931).

[7] P. Debye, Ann. d. Physik **46**, 809 (1915).

[8] R. Wierl, Ann. d. Physik [5] **13**, 453 (1932); L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci. **19**, 68 (1933).

[9] N. F. Mott, Proc. Roy. Soc. (London) **A127**, 658 (1930).

[10] R. W. Dornte, J. Chem. Phys. **1**, 566 (1933).

The diffraction maxima were determined on the microphotometer records of the diffraction rings. Fig. 1 shows typical microphotometer curves of the electron diffraction photographs. The abscissae of these curves were enlarged twofold so that the "bumps" indicating the diffraction maxima were more pronounced in the small scale of the figure.

In Table I are recorded the X values of the diffraction maxima calculated for definite molecular models, the experimentally determined values of $(\sin\theta/2)/\lambda$ for each maxima and l the corresponding C−X interatomic distance in A. The selection of a molecular model depends upon the concordance of the observed diffraction maxima with those calculated for different models. This correlation of calculated and observed maxima is measured by the constancy of the l values; the most probable structure of the molecule gives the smallest deviations in the values of l.

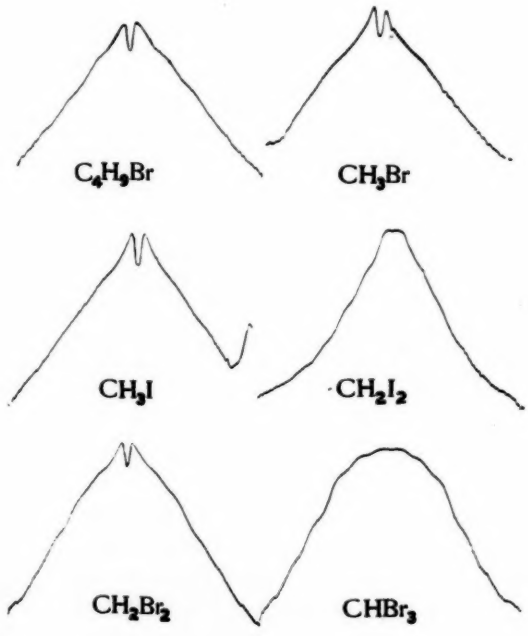

FIG. 1. Microphotometer curves of electron diffraction photographs.

TABLE I.

X	$(\sin\theta/2)/\lambda$	l(C−X in A)
	Tert. Butyl Bromide	
5.65	0.219	2.05
9.75	.376	2.06
14.15	.546	2.06
18.75	.714	2.09
22.50	.872	2.05
	C−C = 1.55±0.05A	
	C−Br = 2.06±0.05A	
	Methyl Bromide	
7.15	0.276	2.06
14.70	.570	2.05
20.55	.791	2.07
	C−Br = 2.06±0.05A	
	Methyl Iodide	
7.25	0.252	2.29
14.50	.512	2.25
20.50	.707	2.31
	C−I = 2.28±0.05A	

$\frac{\sin\theta/2}{\lambda}$	110° X	110° l, (A)	125° X	125° l, (A)	135° X	135° l, (A)
			Methylene Iodide			
0.150	4.75	2.52	4.30	2.28	4.15	2.20
.273	8.55	2.49	7.80	2.27	7.60	2.22
.400	12.75	2.55	11.50	2.29	11.00	2.19
.519	15.75	2.41	14.90	2.28	14.30	2.19
.649	19.75	2.42	18.70	2.29	17.80	2.18
			C−I = 2.28±0.05A			
			I−I = 4.06±0.10A			
			∠I−C−I = 125±5°			
			Methylene Bromide			
0.166	4.75	2.28	4.25	2.04	4.15	1.99
.305	8.50	2.22	7.80	2.03	7.70	2.01
.452	12.75	2.24	11.55	2.03	11.05	1.94
.574	16.20	2.24	14.75	2.04	14.30	1.98
.738	20.25	2.18	18.75	2.02	17.90	1.93
			C−Br = 2.03±0.05A			
			Br−Br = 3.61±0.10A			
			∠Br−C−Br = 125±5°			

$\frac{\sin\theta/2}{\lambda}$	110° X	110° l, (A)	115° X	115° l, (A)	120° X	120° l, (A)
			Bromoform			
0.181	4.80	2.11	4.65	2.04	4.45	1.96
.324	8.50	2.09	8.35	2.05	8.10	1.99
.473	12.60	2.12	12.20	2.05	11.85	1.98
.612	16.25	2.11	15.75	2.05	15.35	2.00
.756	20.25	2.13	19.75	2.07	19.10	2.01
			C−Br = 2.05±0.05A			
			Br−Br = 3.46±0.10A			
			∠Br−C−Br = 115±2°			

Discussion

In the interpretation of the electron diffraction pictures of tertiary butyl bromide the effect of the hydrogen atoms has been neglected so that Eq. (1) becomes

$$\frac{I}{k}=2Z_C Z_{Br}\left(\frac{\sin X}{X}+3\frac{\sin 1.43X}{1.43X}\right)+6Z_C^2\left(\frac{\sin 0.75X}{0.75X}+\frac{\sin 1.23X}{1.23X}\right)+4Z_C^2+Z_{Br}^2. \quad (2)$$

Eq. (2), shown in Fig. 2, gives a satisfactory correlation of the diffraction maxima and indicates a 110° angle between the bonds of the tertiary carbon atom. The distance between the tertiary carbon atom and the methyl carbon atoms is 1.55A; the separation of the methyl carbon atoms is 2.53A; the methyl carbon to bromine interatomic distance is 2.94A.

In the analysis of the diffraction pictures of methyl bromide and iodide the scattering of the hydrogen atoms has been considered although their effect causes only very slight deviations of the intensity curves from the simple $(\sin X)/X$ form, characteristic of a single interatomic distance. The inclusion of the effect of the hydrogen atoms gives a slightly better result for the carbon-halogen interatomic distance. Since the position of the hydrogen atoms cannot be determined by the diffraction experiments, the carbon-hydrogen distance was taken as 1.08A. The relative intensity expression for methyl bromide is

$$\frac{I}{k}=2Z_C Z_{Br}\frac{\sin X}{X}+6Z_H Z_{Br}\frac{\sin 1.28X}{1.28}+6Z_H Z_C\frac{\sin 0.53X}{0.53X}+3Z_H^2+Z_C^2+Z_{Br}^2. \quad (3)$$

The carbon-bromide distance was found to be 2.06A. For methyl iodide the relative intensity equation is

$$\frac{I}{k}=2Z_C Z_I\frac{\sin X}{X}+6Z_H Z_I\frac{\sin 1.24X}{1{\cdot}24X}+6Z_H Z_C\frac{\sin 0.47X}{0.47X}+3Z_H^2+Z_C^2+Z_I^2, \quad (4)$$

which gives a carbon-iodine distance of 2.28A in agreement with the value found in ethyl iodide 2.32A.[11]

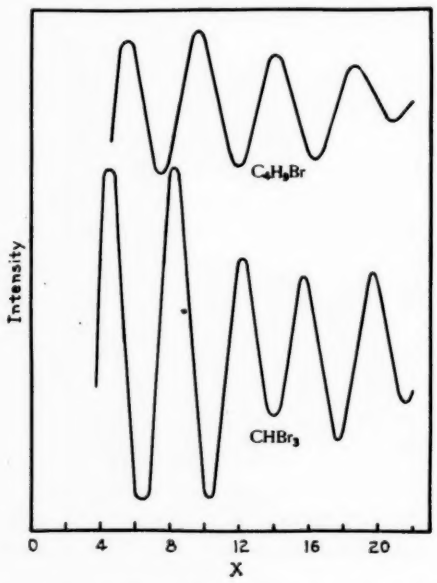

Fig. 2. Theoretical intensity curves for tert. butyl bromide and bromoform with 115° between the C−Br bonds.

The scattering effect of the hydrogen atoms in methylene iodide and bromide may be omitted without any appreciable error in the analysis of the diffraction pictures. On this basis the problem is simplified to a consideration of triatomic molecular structures. For methylene iodide Eq. (1) becomes

$$\frac{I}{k}=4Z_C Z_I\frac{\sin X}{X}+2Z_I^2\left(1+\frac{\sin aX}{aX}\right)+Z_C^2, \quad (5)$$

in which a is a parameter characteristic of the angle between the carbon-iodine bonds and has the values 1.63, 1.78 and 1.85 for the angle 110°, 125° and 135°, respectively. The data of Table I clearly show the best correlation of observed and calculated maxima for an angle of 125°. The distance between the carbon and iodine atoms is 2.28A and the separation of the iodine atoms is

[11] L. Bru, Anales soc. espan. fis. quim. **31**, 115 (1933).

4.06A. For methylene bromide the relative intensity equation is

$$\frac{I}{k}=4Z_C Z_{Br}\frac{\sin X}{X}+2Z_{Br}^2\left(1+\frac{\sin aX}{aX}\right)+Z_C^2, \quad (6)$$

in which a is now characteristic of the angle between the carbon-bromine bonds and has the same values as in Eq. (5). Fig. 3 shows the relative intensity curves of three cases considered for methylene bromide. Here, also, the correlation is best for an angle of 125° which corresponds to a bromine-bromine interatomic distance of 3.61A.

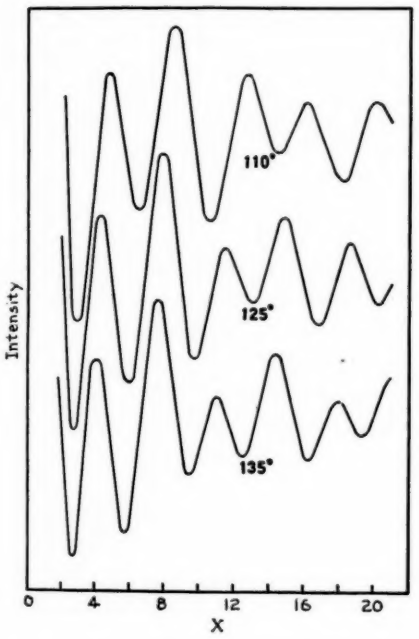

FIG. 3. Theoretical intensity curves for methylene bromide with 110°, 125° and 135° angle between the C—Br bonds.

The uncertainty in the determination of the angle is ±5°. In 1, 1 dibromo ethane the bromine separation was found to be 3.56A[12] in agreement with the value for methylene bromide.

For bromoform Eq. (1) becomes

$$\frac{I}{k}=6Z_C Z_{Br}\frac{\sin X}{X}+6Z_{Br}^2\frac{\sin aX}{aX}+Z_C^2+3Z_{Br}^2 \quad (7)$$

where a is characteristic of the angle between the carbon-bromine bonds and has the values 1.63, 1.68 and 1.73 for the angles 110°, 115° and 120° respectively. Fig. 2 shows Eq. (7) for an angle of 115° which gives the best correlation of maxima. The distance between the bromine atoms of bromoform is 3.46A.

The present results on methylene bromide and iodide together with previous results on methylene chloride[3] indicate that the angle between the carbon-halogen bonds of methane derivatives containing two halogen atoms is practically a constant, 125°. In the tri-substituted methanes the angle between the carbon-halogen bonds is 115° for chloroform[3] and bromoform. An estimate of this angle in iodoform can be made from the x-ray analysis of crystalline iodoform by Huggins and Noble[13] who found 3.56A for the distance between iodine atoms of the same molecule and reported 3.80A as found by Brockway and Pauling for iodoform in benzene solutions. The latter value, which is preferable for comparison with results from experiments with gases, leads to a value around 115° in agreement with results for chloroform and bromoform.

[12] R. Wierl, Ann. d. Physik [5] **13**, 453 (1932).

[13] M. L. Huggins and B. A. Noble, Am. Mineral **16**, 519 (1931).

The Crystal Lattice of Sodium Bicarbonate, $NaHCO_3$

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I. INTRODUCTION

SOME time ago we started in this laboratory crystal structure examinations of the bicarbonates of ammonium, potassium and sodium. The investigations were undertaken in the hope that some results might be obtained concerning the rôle which the hydrogen atoms play in salts of polybasic acids.

The ammonium compound is orthorhombic and some preliminary results obtained on this crystal have already been published from this laboratory.[1] The bicarbonates of potassium and sodium are monoclinic, but not isomorphous with each other.

Crystals of sodium bicarbonate are described in Groth, *Chemische Krystallographie*.[2] The symmetry is given as monoclinic prismatic with the following elements:

$$a : b : c = 0.7645 : 1 : 0.3582 \qquad \beta = 93° 19'.$$

There is a perfect cleavage parallel to the (101) face, a rather perfect one parallel to the (111) face and an imperfect cleavage parallel to (100).

By slow evaporation of aqueous solutions I obtained small but excellent crystals of $NaHCO_3$. They were needle-shaped parallel to the crystallographic c-axis. Twinned crystals were often observed; the two individuals having the (101) face in common. Dr. Tom. Barth of the Geophysical Laboratory was kind enough to examine my crystals optically. He found that the birefringence was strong and negative in character. The refractive indices were found to be:

$$\alpha = 1.38 \pm 0.01 \qquad \beta = 1.50 \pm 0.01 \qquad \gamma = 1.58 \pm 0.01.$$

The plane of the optical axes is (010), $2V$ being 102°. The acute bisectrix is exactly normal to the cleavage plane (101). More accurate values for the refractive indices are:

$$\alpha = 1.380 \qquad \beta = 1.500 \qquad \gamma = 1.586.^3$$

All the x-ray observations were taken on one crystal of approximate dimensions $0.3 \times 0.2 \times 1.0$ mm. A series of Laue photographs and a large number of oscillation photographs were taken. The Laue photographs served merely as a check on the size of the unit cell, as the intensity considerations were based entirely on the observations obtained from the oscillation photographs. For the latter Mo $K\alpha$ radiation was used. The wave-length of the $\alpha_1\alpha_2$ doublet was taken to be 0.7095A. The angle through which the crystal was oscillated was for all exposures 15°. Reflections from some 300 different planes were recorded on the photographs.

II. UNIT CELL AND SPACE GROUP

The dimensions of the unit cell were found to be:

$$a = 7.51 \pm 0.04\text{A} \qquad c = 3.53 \pm 0.03\text{A}$$
$$b = 9.70 \pm 0.04\text{A} \qquad \beta = 93° 19'.$$

The cell dimensions correspond to the axial ratios 0.774 : 1 : .364.

The density is given by Groth as 2.221, in *International Critical Tables* as 2.20. Consequently there are four molecules of $NaHCO_3$ in the unit cell. The calculated density is 2.16 ± 0.04.

According to the observed symmetry the space group must belong to the monoclinic prismatic class. As reflections from planes for which $h+k$ and $k+l$ are odd have been observed, the translation lattice is simple monoclinic.

Reflections hOl are absent if $h+l$ is odd and reflections OkO are absent in odd orders. Consequently the symmetry plane is a glide plane with translations $a/2+c/2$ rather than a reflection plane, and the twofold axis is a screw axis

[1] R. C. L. Mooney, Phys. Rev. **39**, 861 (1932).

[2] P. v. Groth, *Chemische Krystallographie* **II**, 191, Leipzig, 1908.

[3] H. Brasseur, Zeits. f. Krist. **83**, 493 (1932).

rather than a simple rotation axis. Because of the large number of atoms in the unit cell, it may be safely assumed that at least some of them occupy general positions in the space group. It follows that the correct space group is $P2_1/n(C_{2h}^5)$.

The positions of this space group referred to a center of symmetry as origin become:

Centers of symmetry:

$(000)(\frac{1}{2}0\frac{1}{2})$, $(\frac{1}{2}00)(00\frac{1}{2})$, $(0\frac{1}{2}0)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}\frac{1}{2}0)(0\frac{1}{2}\frac{1}{2})$

General positions: $\pm(xyz)\pm(x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2})$.

The expression for the structure amplitude for atoms in general positions becomes:

$h+k+l$ even

$$F=4\Sigma f_n \cos(h2\pi x+l2\pi z)\cos 2\pi yk \qquad (1)$$

$h+k+l$ odd

$$F=-4\Sigma f_n \sin(h2\pi x+l2\pi z)\sin 2\pi yk. \qquad (2)$$

III. Determination of the Structure

The probable number of degrees of freedom in the structure is 15. In general it is not a hopeless task to determine uniquely an atomic arrangement containing 15 degrees of freedom. It was soon found out, however, that in the present case a direct attack on the structure would lead to extreme difficulties. This circumstance was caused by the fact that all the atoms (neglecting the hydrogen atoms) have appreciable values of the scattering power over the entire range of observations, and also by the fact that all intensities of reflection occurring at small values of $\sin\theta/\lambda$ were relatively weak.

It is safe to make the assumption that CO_3-groups exist in the atomic arrangement. The dimensions of the CO_3-group are known rather accurately from previous structure determinations on other carbonates. The group has the shape of an equilateral triangle with the carbon atom at the center and the three oxygen atoms at the corners. The distance from carbon to oxygen is about 1.27A. Because of the strong forces inside the CO_3-group there can be only negligible differences in dimensions as we pass from one crystal to another. I wish to emphasize the fact that in the present case there is no danger in making assumptions of this kind, even if the assumptions should not happen to be correct. The scattering powers of oxygen as well as of carbon are of the same order of magnitude as that of sodium and it would therefore be impossible to obtain agreement with the observed intensities for a large number of reflections if the assumptions were incorrect. The existence of CO_3-groups necessitates that the carbon atoms as well as the oxygen atoms occupy general positions of the space group. Hence the number of parameters for the carbon and oxygen atoms is 12.

It follows from the optical properties that the CO_3 groups are oriented with their planes parallel to the cleavage face (101) (or very nearly so). In this manner we have reduced the number of parameters for the carbon and oxygen atoms from 12 to 4. Three parameters fix the position of the carbon atom and a fourth one takes care of the rotation of the whole group in the (101) plane.

Let $x_1y_1z_1$ be the coordinates of the carbon atom expressed in fractions of the cell dimensions and let χ be the parameter fixing the rotation of the whole CO_3-group in the (101) plane. The value $\chi=0°$ corresponds to the following orientation of the group: One edge of the equilateral triangle is parallel to the (010) face, the opposite corner of the triangle pointing in the positive direction of the b-axis. For the sake of convenience we introduce new parameters defined by the relations:

$$\varphi_1=2\pi x_1 \qquad \varphi_2=2\pi y_1 \qquad \varphi_3=2\pi z_1.$$

The determination of the atomic arrangement was now made in the following straightforward but rather laborious way. The contribution of the CO_3 group to the amplitude for reflections hkO depends only upon φ_1, φ_2 and χ. This contribution was calculated as function of φ_1, φ_2 and χ for a large number of reflections hkO. Calculations were made for 5° intervals in φ_1 and φ_2 and for intervals of $7\frac{1}{2}°$ in χ.

The contribution from the sodium atoms to the structure amplitudes of the same reflections hkO was next calculated on the assumption that the sodium atoms were situated at centers of symmetry. Adding together the contributions we found, however, that agreement with observed intensities could not be obtained for any

set of values $\varphi_1\varphi_2\chi$. It was consequently concluded that the sodium atoms have to lie in general positions, characterized by coordinates $x_2y_2z_2$. Again we will introduce new parameters defined by the relations $\psi_1=2\pi x_2$ $\psi_2=2\pi y_2$ $\psi_3=2\pi z_2$.

The contribution from the sodium atoms to the structure amplitude for reflections *hkO* was then calculated as function of ψ_1 and ψ_2. The calculations were made for intervals of 5° in ψ_1 and ψ_2.

Combining now the contributions from the CO_3 groups and the sodium atoms it was found that agreement with observations could be obtained only for one set of values $\varphi_1\varphi_2\chi\psi_1\psi_2$, namely the following:

$$\varphi_1=25° \quad \varphi_2=85° \quad \chi=0°$$
$$\psi_1=100° \quad \psi_2=0°$$

The remaining two parameters, φ_3 and ψ_3, which fix the translation of the sodium and carbon atoms in the direction of the *c*-axis, can then be determined very easily and one finds:

$$\varphi_3=113° \quad \psi_3=255°.$$

TABLE I. *Observed intensities and calculated amplitudes.*

hkl	sin θ/λ	*I*	*F*	*hkl*	sin θ/λ	*I*	*F*	*hkl*	sin θ/λ	*I*	*F*	*hkl*	sin θ/λ	*I*	*F*
110	0.0843	w	− 6	420	0.2860	w	20	32$\bar{2}$	0.3540	w	−12	46$\bar{1}$	0.4278	nil	3
020	.1031	ms	−13	241	.2872	nil	7	14$\bar{2}$	.3545	nil	− 7	630	.4290	nil	0
120	.1228	w	− 4	340	.2873	m	−18	50$\bar{1}$	.3554	w	16	37$\bar{1}$	.3329	w	−18
200	.1333	w	−10	012	.2887	vw	14	232	.3555	nil	− 2	280	.4334	w-	−12
210	.1430	s	−22	250	.2902	vw	4	351	.3600	nil	0	103	.4348	nil	− 2
011	.1511	m	− 9	11$\bar{2}$	.2929	s	39	142	.3601	w	−16	26$\bar{2}$	.4360	ms	34
10$\bar{1}$	.1537	m	−32	051	.2943	w	−17	44$\bar{1}$	.3603	nil	3	081	.4362	nil	− 2
101	.1601	s-	−35	331	.2951	nil	0	26$\bar{1}$	.3628	w	13	461	.4370	nil	6
11$\bar{1}$	.1621	s-	29	112	.2997	nil	− 9	170	.3670	w	−13	113	.4378	nil	− 1
111	.1682	vs	−50	41$\bar{1}$	.2999	s	−42	530	.3675	m	−32	352	.4395	nil	9
130	.1684	s-	−22	15$\bar{1}$	.3001	nil	− 6	261	.3683	w	− 5	371	.4398	nil	− 2
220	.1686	s	−40	022	.3022	w-	−17	360	.3684	w	−14	18$\bar{1}$	.4401	vw	−18
021	.1755	vw	− 6	151	.3034	m	24	501	.3692	w-	23	181	.4424	w	19
12$\bar{1}$	.1851	s	−31	12$\bar{2}$	.3062	vw	13	450	.3709	m-	−17	262	.4452	w	22
121	.1904	vs	64	20$\bar{2}$	.3074	m-	25	441	.3712	w	10	123	.4469	w	−24
21$\bar{1}$	.1965	nil	5	430	.3083	nil	− 3	33$\bar{2}$	.3723	s	−41	470	.4487	m	28
230	.2042	vvw	− 3	060	.3093	vs	57	40$\bar{2}$	.3792	w	−23	640	.4500	nil	− 6
040	.2062	nil	− 1	21$\bar{2}$	.3117	w-	2	242	.3808	m	22	28$\bar{1}$	.4539	w	−18
211	.2064	vw	− 4	122	.3127	nil	9	052	.3836	nil	− 1	560	.4547	w-	−10
310	.2065	w	9	42$\bar{1}$	.3129	nil	− 7	270	.3847	w	10	281	.4583	nil	− 1
031	.2100	vw-	− 2	411	.3130	s	29	15$\bar{2}$	.3868	w	16	380	.4584	m-	20
22$\bar{1}$	.2158	s	−44	34$\bar{1}$	.3158	m-	25	071	.3878	nil	− 2	36$\bar{2}$	.4587	w-	2
140	.2167	vw	11	160	.3164	vw	− 9	332	.3881	w-	− 4	072	.4592	nil	− 8
13$\bar{1}$	.2180	nil	2	25$\bar{1}$	.3200	w	14	36$\bar{1}$	.3910	w-	− 4	133	.4615	nil	0
131	.2226	nil	1	202	.3202	m-	33	152	.3919	w	−14	17$\bar{2}$	.4619	m	30
221	.2249	vw-	− 2	032	.3235	vvw	1	540	.3920	w	−10	172	.4662	nil	− 4
320	.2250	vs	48	22$\bar{2}$	.3242	w-	10	451	.3921	w-	10	47$\bar{1}$	.4664	s-	−30
30$\bar{1}$	.2391	w	14	212	.3242	ms	48	17$\bar{1}$	.3923	w-	−13	190	.4688	w-	−12
31$\bar{1}$	.2446	w	− 6	341	.3251	w	−17	171	.3948	w	− 8	710	.4695	w-	15
23$\bar{1}$	.2447	s	38	421	.3255	w	−19	34$\bar{2}$	.3965	vw	4	362	.4716	vw	12
240	.2456	s	−36	251	.3262	m-	−25	361	.3986	vw	−19	27$\bar{2}$	.4740	vw	− 2
041	.2504	ms	22	350	.3263	m-	14	402	.3998	w-	− 6	471	.4749	m-	21
301	.2514	vs	−57	13$\bar{2}$	.3272	w	−16	600	.4000	m	−33	650	.4759	vw	2
231	.2528	vw-	10	132	.3333	vw-	− 5	25$\bar{2}$	.4012	nil	1	38$\bar{1}$	.4767	m	31
330	.2528	s	30	43$\bar{1}$	.3335	nil	7	451	.4022	w-	10	720	.4780	nil	0
311	.2566	nil	3	222	.3364	w	23	610	.4033	vw	−11	60$\bar{2}$	.4782	vw	8
14$\bar{1}$	.2572	s	−28	260	.3368	m	−26	27$\bar{1}$	.4077	nil	3	143	.4812	w-	−15
32$\bar{1}$	.2604	w	29	440	.3371	w	19	460	.4084	m	20	272	.4824	nil	7
141	.2610	s	51	510	.3373	w-	−10	252	.4110	w	−32	290	.4828	w-	−11
150	.2663	m	20	061	.3403	w	−18	342	.4114	w-	−12	381	.4830	m	−30
400	.2667	w	27	31$\bar{2}$	.3426	w-	− 8	080	.4124	m	22	091	.4853	nil	0
410	.2716	vw-	8	23$\bar{2}$	.3441	nil	0	271	.4125	nil	6	19$\bar{1}$	.4888	w-	14
321	.2717	w	−19	43$\bar{1}$	.3453	w	−17	370	.4126	vw	6	191	.4908	vw	− 8
24$\bar{1}$	.2802	m-	24	16$\bar{1}$	.3454	m-	−23	620	.4130	vw	− 2	480	.4912	vw	9
002	.2841	s	−41	161	.3482	vw	5	180	.4178	vw	− 1	570	.4913	nil	− 3
33$\bar{1}$	.2848	nil	2	520	.3489	w	21	062	.4199	w-	−14	730	.4917	m-	25
042	.3510	w	−18	35$\bar{2}$	.4256	w	−20	550	.4214	m-	−17	37$\bar{2}$	.4949	nil	− 2
35$\bar{1}$	.3516	w-	10	162	.4276	w-	15	16$\bar{2}$	.4229	nil	− 4	701	.4950	nil	− 5

The final coordinates of all the atoms are given in Table II. The correctness of our initial assumptions concerning the CO_3 groups are adequately proved by the fact that good agreement between observed and calculated intensities is obtained. Changes in the size of the CO_3-group do not seem to improve the agreement.

The *f*-curves used in the calculations are given in Table III. In agreement with modern conceptions of the binding inside the CO_3-group I have assumed the states of ionization as C^{+1} and O^{-1}.

When one compares the calculated structure amplitudes, *F*, with the observed intensities, *I*, in Table I, the following facts should be kept in mind. If the crystal is of the mosaic type the intensity is proportional to the square of the amplitude, while for ideally perfect crystals the intensity is proportional to the amplitude itself. Aside from the structure amplitude the intensity depends upon a series of factors. The polarization factor, the Lorentz factor and the temperature factor changes continually with increasing values of $\sin\theta/\lambda$. Hence they can be left out of consideration if we compare intensities of reflections occurring at similar values of $\sin\theta/\lambda$. The absorption can safely be disregarded too, because of the low absorption coefficient and because we used a very small crystal.

TABLE II. *Final parameter values.*

	In angular measure			In fractions of cell dimensions		
	$2\pi x$	$2\pi y$	$2\pi z$	x	y	z
Na	100°	0°	255°	0.278	0	0.708
C	25°	85°	113°	.069	0.236	.314
O_I	25°	132°	113°	.069	.367	.314
O_{II}	72°	61°	66°	.200	.169	.183
O_{III}	338°	61°	160°	.939	.169	.444
H	115°	90°	23°	.319	.250	.064

TABLE III. *The scattering powers.*[4]

$\sin\theta/\lambda$	0	0.10	0.20	0.30	0.40	0.50	0.60	0.70
Na^{+1}	10	9.5	8.3	6.9	5.4	4.1	3.2	2.6
C^{+1}	5	3.6	2.5	2.0	1.9	1.7	1.6	1.4
O^{-1}	9	7.9	5.9	4.2	2.9	2.2	1.8	1.6

IV. Discussion of the Structure

A projection of the atomic arrangement is reproduced in Fig. 1.

[4] James and Brindley, Zeits. f. Krist. **78**, 470 (1931).

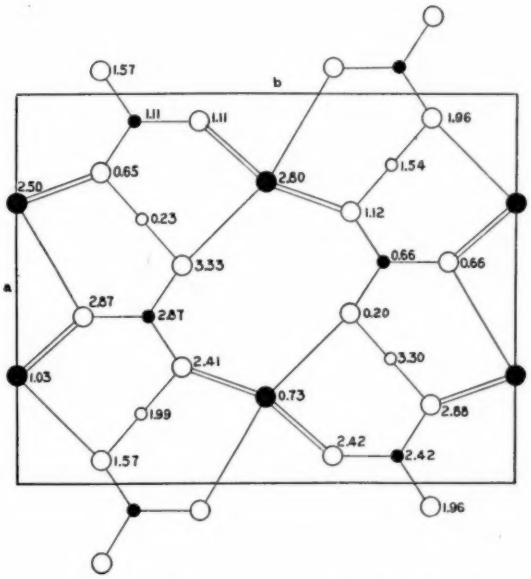

FIG. 1. The atomic arrangement in sodium bicarbonate. The figure shows the atomic arrangement viewed along the *c*-axis. Large open circles represent oxygen atoms, large filled circles sodium atoms, small open circles hydrogen atoms and small filled circles represent the carbon atoms. Bonds between atoms are indicated by connection lines. The attached numbers represent the heights in A above the *c*-face. It should be remembered that since the crystal is monoclinic the *c*-face is not normal to the *c*-axis. In the figure the *c*-face passes through the two horizontal edges, of which the upper one lies in the plane of the paper, while the lower one lies below the plane of the paper an amount 0.43A.

Each sodium atom is surrounded by 6 oxygen atoms in the first sphere of coordination. Of these six oxygen atoms three are of the type O_I, two are of the type O_{II}, while there is only one of the type O_{III}. The distance from sodium to the different oxygen atoms is:

Na−O_I	2.55A	Na−O_{II}	2.44A
−O_I	2.37A	−O_{II}	2.53A
−O_I	2.57A	−O_{III}	2.35A

The average Na−O distance is thus 2.47A, which compares favourably with the value 2.44A calculated on the basis of the ionic radii published by the author.[5] Goldschmidt's[6] and Pauling's[7] values for the Na−O distance are 2.30A and 2.35A, respectively. In other crystals where sodium occurs with coordination number six,

[5] W. H. Zachariasen, Zeits. f. Krist. **80**, 137 (1931).

[6] See V. M. Goldschmidt, Geochem. Verteil. Gesetze d. Elemente **VII**, Vid. Akad. Skr. Oslo (1926).

[7] L. Pauling, J. Am. Chem. Soc. **49**, 763 (1927).

the following Na−O values have been found: In $NaClO_3$ 2.46A,[8] in $NaNO_2$ 2.48A,[9] in Na_2SO_4 2.41A.[10]

For the distance between oxygen atoms belonging to different CO_3 groups we get the following values: 2.55A, 3.12A, 3.15A, 3.19A.

V. The Hydrogen Bonds

The positions of the hydrogen atoms cannot be found from intensity calculations. Their location in the atomic arrangement, however, can be found by very simple considerations.

Whereas the binding within the carbonate group presumably comes closer to the valence type than to the ionic type, it must be assumed that the bonds between sodium and oxygen atoms are chiefly ionic in character. This conclusion is confirmed by the fact that the coordination number around sodium as well as the observed sodium to oxygen distance can be correctly calculated from the (univalent) ionic radii of 0.98A and 1.76A for Na^+ and O^{-2}.[4] The effective radius of the oxygen ion in the coordination sphere around sodium is 1.57A. (Compare the author's paper on ionic radii.) The smallest distance to expect between two oxygen ions in the coordination sphere around sodium is consequently 3.14A. All the oxygen to oxygen distances except the one of 2.55A between an O_{II} and an O_{III} atom are in harmony with this result. The small distance of 2.55A has to be attributed to the fact that additional binding forces are operative between oxygen atoms O_{II} and O_{III}. This additional binding has to be ascribed to the presence of a hydrogen atom (ion). We thus come to the conclusion that the hydrogen atoms are located halfway between oxygen atoms O_{II} and O_{III}, forming a group O−H−O with a distance of 1.275A between a hydrogen and an oxygen atom.

One gets additional support for this location of the hydrogen atoms by applying Pauling's principle of balanced valence.[11] The sum of the strength of the sodium and carbon bonds ending upon the different kinds of oxygen atoms are 1.83 for O_I, 1.67 for O_{II} and 1.50 for O_{III}. In order to bring the total sum of the bond strengths for each oxygen atom as close to 2.00 as possible it becomes necessary to link up the atoms O_{II} and O_{III} each to one hydrogen atom. But this is exactly what we found above in another way. The total bond strengths become 1.83 for O_I, 2.17 for O_{II} and 2.00 for O_{III}.

When we say that the hydrogen atoms lie halfway between two oxygen atoms O_{II} and O_{III}, we mean the time average positions. It is, of course, conceivable that the hydrogen atom part of the time may be closer associated with atom O_{II}, part of the time closer associated with atom O_{III}, i.e., that the hydrogen atom oscillates back and forth between the two oxygen atoms.

In his structure investigation of KH_2PO_4, J. West[12] was led to the conclusion that the hydrogen atoms also in that compound were situated halfway between two oxygen atoms. For the H−O distance West gives 1.27A, in complete agreement with our value. The existence of groups $(O-H-O)^{-1}$ in several silicates has been strongly advocated by L. Pauling from considerations based upon his principle of balanced valence. The H−F distance in the analogous hydrofluoric group $(F-H-F)^-$ is 1.18A.

It may be mentioned that also in boric acid, H_3BO_3, the hydrogen atoms lie halfway between two oxygen atoms.[13] It seems therefore to be a general rule that the hydrogen atoms in crystalline acids and acid salts of oxygen acids form groups (O−H−O), the two oxygen atoms belonging to different radicals. In acids like H_3PO_3 and H_3PO_2 the formulae have to be written as $H_2(HPO_3)$ and $H(H_2PO_2)$, so that compounds $R_2(HPO_3)$ and $R(H_2PO_2)$ are not to be termed acid salts. A compound like $NH_4(HPO_3)H$, however, is a true acid salt, in which there exist groups O−H−O. For bisulphites the formulae probably have to be written as $R(SO_3)H$, although it is conceivable that the hydrogen atom might be attached directly to the sulphur atom, $R(HSO_3)$. Careful x-ray examinations of bisulphites would settle that question.

In the $NaHCO_3$ structure the hydrogen atoms

[8] W. H. Zachariasen, Zeits. f. Krist. **71**, 517 (1929).
[9] G. E. Ziegler, Phys. Rev. **38**, 1040 (1931).
[10] W. H. Zachariasen and G. E. Ziegler, Zeits. f. Krist. **81**, 92 (1932).
[11] L. Pauling, J. Am. Chem. Soc. **51**, 1010 (1929).
[12] J. West, Zeits. f. Krist. **74**, 306 (1930).
[13] From unpublished data by the author.

link the carbonate groups together so as to form endless strings parallel the $[10\bar{1}]$ direction. The strings are furthermore flat, their plane being parallel to the (101) face. It is worth noticing that the crystals show a perfect cleavage parallel to the plane of the strings. The bonds between hydrogen and oxygen atoms are, however, not strong enough to give the crystals a fibrous character.

VI. Summary

Crystals of sodium bicarbonate, $NaHCO_3$, are monoclinic prismatic. The unit cell contains four molecules and has dimensions

$a=7.51\pm0.04$A $b=9.70\pm0.04$A $c=3.53\pm0.03$A

with an angle β of 93° 19′. The calculated density is 2.16 as against 2.20–2.22 observed. The space group is $P2_1/n$.

It was assumed that the lattice contains CO_3-groups of the same shape and dimensions as in other carbonates. The optical properties showed that the carbonate groups were oriented parallel to the (101) face. Starting out from these assumptions all atomic positions (except those for hydrogen) were determined from intensity calculations. The positions of the hydrogen atoms were found from considerations of interatomic distances.

All atoms are lying in general positions in the arrangement: $\pm(xyz)\pm(x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2})$. The values of the 18 parameters involved are:

	x	y	z		x	y	z
Na	0.278	0	0.708	O_{II}	0.200	0.169	0.183
C	0.069	0.236	0.314	O_{III}	0.939	0.169	0.444
O_I	0.069	0.367	0.314	H	0.319	0.250	0.064

Each sodium atom is surrounded by six oxygen atoms at an average distance of 2.47A.

Each hydrogen atom is linked to two oxygen atoms, forming a collinear group O−H−O. The distance H−O is 1.275A. This result is an additional proof that hydrogen is capable of forming two bonds.

In conclusion I wish to thank Dr. Tom. Barth of the Geophysical Laboratory for the optical examination of my crystals.

Calculation of the Refractive Indices of Sodium Bicarbonate from the Atomic Arrangement

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I. INTRODUCTION

IN the following we will attempt to calculate the optical properties of sodium bicarbonate directly from the atomic arrangement given in the preceding article.

Two methods for calculating the refractive indices from the crystal lattice have been described.[1] The crystal lattice of sodium bicarbonate is characterized by as many as 18 degrees of freedom, so that the numerical calculation involved in the Born-Ewald method becomes forbidding, and we will therefore use the Bragg method which is more simple. In spite of the success of Bragg's attempts to account for the optical properties of calcite and aragonite structures, very little attention has been paid to this interesting and useful method. Recently it was tried to find a correlation between prominent optical characters of crystals and striking features in the atomic arrangements.[2] Certain definite relationships were actually established. It is of interest to note that these empirical correlations without exception can be directly and simply deduced by application of Bragg's method, a fact which strangely enough was completely overlooked.

In the following chapter we will give a brief resumé of the principles upon which Bragg based his methods.

II. W. L. BRAGG'S METHOD FOR CALCULATION OF REFRACTIVE INDICES

When a crystal is placed in an electric field it will become polarized, and the well-known relation (1) will hold.

$$EK = E + 4\pi P \tag{1}$$

where E is the intensity of the field, K the dielectric constant and P the total polarization per cc. The total polarization represents the sum of all the induced dipole moments. For not too strong fields the moment induced is proportional to the intensity of the field, the proportionality factor being defined as the polarizability of the particle. Hence we can write

$$P = N\Sigma m = N\Sigma\delta F \tag{2}$$

where N is the number of molecules per cc, Σm the sum of the dipole moments per molecule, δ the polarizability and F the intensity of the field acting upon the particle. The field F consists of the field E and the field due to all the surrounding dipoles in the crystal.

Let us draw a sphere around the particle under consideration sufficiently large to include a great number of polarized atoms, but small enough so that E does not vary appreciably over distances compared with it. All the dipoles lying on or outside this sphere will then be responsible for a field at the center of intensity $4/3\pi P$. The dipoles within the sphere will, however, create a field at the center whose intensity depends upon the spatial arrangement of the dipoles. Suppose that the sphere contains n dipoles $m_1 m_2 \cdots m_n$ with components of moments $m_{1,x}\, m_{1,y}\, m_{1,z}$ up to $m_{n,x}\, m_{n,y}\, m_{n,z}$ and with coordinates $x_1 y_1 z_1$ up to $x_n y_n z_n$. Let subscript one refer to the atom at the center of the sphere which is the origin of our coordinate system. The dipole m_p will produce a field at origin whose intensity in the x-direction is given by:

$$f_{1,p}{}^{x} = \frac{3x_p{}^2 - r_p{}^2}{r_p{}^5} m_{px} + \frac{3x_p y_p}{r_p{}^5} m_{py} + \frac{3x_p z_p}{r_p{}^5} m_{pz}, \tag{3}$$

where r_p is the radius vector, for the y and z components of the created field analogous expressions hold. If now the x-direction is chosen in the di-

[1] M. Born, *Atomtheorie des festen Zustandes*, Leipzig, 1923. W. L. Bragg, Proc. Roy. Soc. (London) **A105**, 370 and **A106**, 346 (1924).

[2] W. A. Wooster, Zeits. f. Krist. **80**, 495 (1931).

rection of the field E, the dipole moments m_1 will be determined by the three equations:

$$m_{1,x}=\delta_{1,x}[E+(4\pi/3)P+\sum_p f_{1,p}{}^x],$$
$$m_{1,y}=\delta_{1,y}\sum_p f_{1,p}{}^y,$$
$$m_{1,z}=\delta_{1,z}\sum_p f_{1,p}{}^z. \quad (4)$$

Analogous equations will hold for all the other dipoles so that we get a system of $3n$ equations. We are interested in finding the x-components of the dipole moments. In order to solve the $3n$ equations of the type (4) the polarizabilities must be known. Let us now suppose that the polarizability of a particle is independent of the direction of the local field, i.e., $\delta_x=\delta_y=\delta_z$ and let us assume that the polarizabilities can be found by other methods. The solutions of Eqs. (4) may then be found and may be given in the form:

$$m=\delta q(E+(4\pi/3)P). \quad (5)$$

Hence the total polarization per unit volume is $P=N\Sigma\delta q(E+(4\pi/3)P)$, which together with Eq. (1) gives us:

$$K-1=n^2-1=4\pi N\Sigma\delta q/(1-(4\pi/3)N\Sigma\delta q). \quad (6)$$

Knowing the polarizabilities we are thus able to calculate the dielectric constants, respectively the refractive indices for infinite wave-lengths. The refractive indices for any given wave-length may be calculated from Eq. (6) provided that we know the polarizabilities for the corresponding frequency.

The optical anisotropy enters through the factors q, which depend upon the atomic arrangement and the orientation of the electric vector, (and also upon the polarizabilities).

III. Application of the Method on Sodium Bicarbonate

In order to carry through the calculations outlined in the previous chapter the polarizabilities of the atoms building up the crystal lattice must be known. We will assume that the polarizabilities of hydrogen and carbon can be considered as negligible. (This assumption does not necessarily imply that we consider carbon to be present as a C^{+4} ion.) The polarizability of an oxygen atom in the $NaHCO_3$ lattice we will take to be the same as for an oxygen atom in carbon dioxide, hence $\delta_0=1.29\times10^{-24}$.[3] For Na^+ we will assume a polarizability of 0.28×10^{-24}, which corresponds to Wasastjerna's mole refraction value for Na^+ in crystals.[4] The polarizability of the sodium ion recently deduced from spectral term values by J. E. Mayer and M. G. Mayer[5] is somewhat lower, namely 0.18×10^{-24}. This latter value, however, refers to a free cation. The polarizabilities given should correspond strictly to Na light.

In order to simplify the numerical calculations the following approximations were made:

I. The sodium ions are polarized to the same extent as if they were in an isotropic medium, i.e., $q_{Na}=1$. This approximation is justified since each sodium ion is surrounded in the first sphere of coordination by six oxygen atoms which occupy the corners of a slightly distorted octahedron. These six oxygen atoms will therefore create a field with negligible intensity in the sodium dipole. The field due to oxygen dipoles still further away will be negligible for the same reason and also because the intensity of the field created by a dipole is inversely proportional to the cube of the distance.

II. For an oxygen dipole we will take into consideration the influence of the surrounding sodium and oxygen dipoles which are less than 5.5A away. In reality this means that we take into account the 35–40 nearest dipoles.

III. Components at right angles to the field will be neglected for all dipoles more than 3.0A away.

As the procedure of the numerical calculations has been discussed in detail in Bragg's original papers, we will give only the results. For information about the atomic arrangement the preceding article should be consulted.

The sodium bicarbonate crystals are monoclinic so that the orientation of the tensor ellipsoid is not completely determined by the symmetry. By actual calculation we were able to show that one of the axes of the ellipsoid is exactly normal to the plane of the CO_3-groups, which are all oriented parallel to each other. It was further

[3] W. L. Bragg, reference 1.

[4] J. H. Wasastjerna, Soc. Scient. Fenn. Comm. Phys. Math. **1**, 37 (1923).

[5] J. E. Mayer and M. G. Mayer, Phys. Rev. **43**, 605 (1933).

found that this axis corresponds to the smallest refractive index, α. The second axis in the ellipsoid because of the monoclinic symmetry must coincide with the twofold axis. This axis corresponds to refractive index β. Thus the symmetry plane must contain the two optical axes. Numerically the calculations gave the following values for the three principal refractive indices: $\alpha=1.393$; $\beta=1.480$; $\gamma=1.583$. Consequently the birefringence is negative in character.

In Table I the calculated and observed optical properties are given:

TABLE I.

Calculated	Observed[6]
Plane containing optical axes is (010)	Plane containing optical axes is (010)
Acute bisectrix normal to (101)	Acute bisectrix normal to (101)
Optically negative	Optically negative
1.393 1.480 1.583	1.380 1.500 1.586
Angle between the optical axes: 92°	Angle between optical axes: 102° (directly observed) 110° (calculated from observed indices)

IV. Discussion of the Results

We wish to emphasize the fact that the calculations were carried out on the basis that the observed values were considered to be completely unknown. That is to say the constants in our equations were not adjusted so as to make the calculated and observed value for one of the refractive indices coincide. It is of interest to note that the calculated and observed orientation of the tensor ellipsoid is exactly the same. The numerical agreement is also as good as may be expected with the approximative character of the method itself.

The differences between observed and calculated refractive indices can only in part be ascribed to our approximations I, II and III. The principal source of inaccuracy no doubt is introduced by the assumption that the polarizability of a particle in the crystal lattice is independent of the direction. Furthermore we have also assumed that all the oxygen atoms in the crystal have the same value for the polarizability in spite of the fact that there actually are three kinds of oxygen atoms. (See the preceding article.)[6]

Most other biaxial carbonates in which the CO_3-groups are parallel are approximately uniaxial (optical axial angle close to 180°, i.e., β and γ nearly equal). This is not true for $NaHCO_3$ and the fact that this abnormal behavior is accounted for by the calculations is worthy of special notice.

Summary

The optical properties of sodium bicarbonate crystals are calculated directly from the known atomic arrangement, when using the method developed by W. L. Bragg.

The results of the calculations and the observed properties are given in Table II.

TABLE II.

	Calculated	Observed
Plane containing optical axes	(010)	(010)
Optical character	Negative	Negative
Direction of acute bisectrix	$\perp$(101)	$\perp$(101)
α	1.393	1.380
β	1.480	1.500
γ	1.583	1.586
$2V$	92°	110°

[6] Compare the preceding article, Zachariasen, J. Chem. Phys. **1**, 634 (1933).

Interatomic Distances in Crystals of the Alkali Halides

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The constants of the empirical repulsion potential assumed by Born and Mayer between two ions, which may be termed the ionic "radii," are calculated for the alkali and halide ions from the lattice constants of the alkali halides. By using 9 such radii the 20 lattice constants can be recalculated nearly within the probable experimental error of their determination. The good agreement is regarded as support for the assumptions involved in the calculations.

INTRODUCTION

CERTAIN equations for the lattice potential in a regular ionic lattice have been developed by Born and Mayer[3] which lead to numerical values[4] of considerable apparent accuracy. The equations imply an empirical repulsive potential between two ions which is a simple exponential function of the distance between the ionic centers and of two constants for each ion. One of these constants, that in the exponent, is assumed to have the same value for all alkali and halide ions and is determined from the compressibilities of the salts.

For any single crystal there then remain two constants, which may be called the radii of the two ions, with only the lattice constant of the crystal (the distance between the centers of closest ions) as one experimental value from which to determine them. This difficulty was not felt in the calculation of the lattice energies, since only the *sum* of the two radii entered in any important way into the calculations and even this was not explicitly determined but eliminated from the equations with the help of the lattice constant. The lattice energies could then be computed from the lattice constant with only a very unimportant assumption concerning the difference between the radii of the two component ions.

The equations used, however, imply that the 20 lattice constants of the 20 alkali halides can be determined by the use of 9 radii, one for each of the alkali and halide ions. The purpose of this paper is to determine these 9 radii and from them recalculate the lattice constants. The excellent agreement obtained with the experimental values offers considerable support to the assumptions of the theory. Deviations from additivity of the lattice constants due to difference in structure type and in the relative sizes of the ions are quantitatively calculated.

METHOD AND RESULTS

It is assumed that the repulsive potential $b(r)$ between two ions i and j, at a distance apart r_{ij}, is given by

$$b(r) = c_{ij} b b_i b_j e^{-r_{ij}/\rho} = c_{ij} b e^{(r_i + r_j - r_{ij})/\rho} \tag{1}$$

in which $\rho = 0.345 \times 10^{-8}$ cm, an empirically determined constant, b is arbitrarily chosen to have the value 10^{-12} erg, and r_i and r_j are what shall be termed the radii of the ions i and j. c_{ij} is a factor calculated by Pauling[5] which gives the dependence of the repulsion on the charges of the ions. It has the value 1.00 for one alkali and one halide ion, 0.75 for two halide ions and 1.25 for two alkali ions, except in the cases of the lithium halides for which the values are 1.375, 0.75 and 2.00, respectively.

[1] Johnston Scholar in Chemistry.

[2] Most of the work here reported was carried out independently by the two authors.

[3] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

[4] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932).

[5] L. Pauling, Zeits. f. Krist. **67**, 377 (1928).

The average potential on a given ion in a crystal composed of univalent ions symmetrically surrounded, as in the NaCl and CsCl type structures, can be written

$$\Phi(r)=A(r)+B(r), \tag{2}$$

in which $A(r)$, the attractive potential, and $B(r)$, the repulsive potential, are given by the following equations:

$$A(r)=-\alpha e^2/r-C/r^6-D/r^8, \tag{3}$$

$$B(r)=B_{+-}(r)+[B_{--}(r)+B_{++}(r)]/2, \tag{4}$$

$$B_{+-}(r)=bc_{+-}Me^{(r_++r_--r)/\rho}, \tag{5}$$

$$[B_{--}(r)+B_{++}(r)]/2=[bc_{--}M'e^{(2r_--ar)/\rho}+bc_{++}M'e^{(2r_+-ar)/\rho}]/2$$

$$=bc_{+-}Me^{(r_++r_--r)/\rho}[(S/a)e^{-(a-1)r/\rho}], \tag{6}$$

$$S=(c_{--}/c_{+-})(M'/2M)a[1+(c_{++}/c_{--})e^{-2\delta/\rho}]e^{\delta/\rho}. \tag{7}$$

α is Madelung's constant (1.7476 for the NaCl type, 1.7626 for the CsCl type), C and D are van der Waals constants calculated by Mayer,[6] M and M' are the numbers of unlike and like neighbors of each ion, respectively (6 and 12 for the NaCl type, 8 and 6 for the CsCl type). a is the ratio of the distance between like neighbors to that (r) between unlike neighbors ($2^{\frac{1}{2}}$ for the NaCl type, $2/3^{\frac{1}{2}}$ for the CsCl type). δ is the radius difference, r_--r_+.

The first derivative with respect to r is given by

$$d\Phi(r)/dr=(1/r)(\alpha e^2/r+6C/r^6+8D/r^8)-(bc_{+-}M/\rho)e^{(r_++r_--r)/\rho}[1+Se^{-(a-1)r/\rho}]. \tag{8}$$

At equilibrium at zero pressure and at the absolute temperature T, $r=r_0$ and

$$r_0[d\Phi(r_0)/dr]=(3T/N\beta)(\partial V/\partial T)_P=(3T/\beta)\cdot(V/N)\cdot(1/V)(\partial V/\partial T)_P. \tag{9}$$

V/N is the molecular volume, β the coefficient of compressibility and $1/V(\partial V/\partial T)_P$ the coefficient of expansion. Combining Eqs. (8) and (9) we obtain

$$e^{(r_++r_-)/\rho}=e^{r_0/\rho}(\tau/r_0)/(bMc_{+-}/\rho)(1+Se^{-(a-1)r_0/\rho}), \tag{10}$$

$$\tau=\alpha e^2/r_0+6C/r_0^6+8D/r_0^8-(3T/N\beta)(\partial V/\partial T)_P. \tag{11}$$

By taking logarithms to the base 10,

$$(r_++r_-)=r_0+2.303\rho\log_{10}(\tau/r_0)-2.303\rho\log_{10}(bMc_{+-}/\rho)-2.303\rho\log_{10}(1+Se^{-(a-1)r_0/\rho}). \tag{12}$$

All the quantities entering into the terms on the right side of this equation are known except the radius difference δ in the factor S. We can guess a first approximation for the δ values, for instance (following Born and Mayer) taking them equal to the difference between the ionic radii calculated by Goldschmidt.[7] From the (r_++r_-) values obtained on this assumption a set of individual r_+ and r_- values are calculated, and from these new δ values. This process is continued until the assumed radii (Table I) give values which lead to (r_++r_-) values consistent

TABLE I. *Basic radii and repulsion constants.*

	r_+ (10^{-8} cm)	b_+		r_- (10^{-8} cm)	b_-
Li^+	0.475	3.962			
Na^+	0.875	12.63	F^-	1.110	24.96
K^+	1.185	31.02	Cl^-	1.475	71.9
Rb^+	1.320	45.87	Br^-	1.600	103.3
Cs^+	1.455	67.85	I^-	1.785	176.6

[6] J. Mayer, J. Chem. Phys. **1**, 270 (1933).

[7] V. Goldschmidt, Skrifter Norske Videnskaps, Akad. Oslo, 1926, Nos. 7 and 8; Ber. d. deutsch chem. Ges. **60**, 1263 (1927).

TABLE II.

1	2[8]	3[6]	4[6]	5	6	7	8	9
Formula	r_0 (exp.) $\times 10^8$ cm	C $\times 10^{60}$ erg cm^6	D $\times 10^{76}$ erg cm^8	β $\times 10^{12}$ bar	$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ $\times 10^5$ grad^{-1}	$\frac{\alpha e^2}{r_0}$ $\times 10^{12}$ erg	$\frac{6C}{r_0^6}+\frac{8D}{r_0^8}$ $\times 10^{12}$ erg	$\frac{3T}{N\beta}\left(\frac{\partial V}{\partial T}\right)_{P=0}$ at $T=298°$ $\times 10^{12}$ erg
LiF	2.01_0	18	11	1.53^9	9.2^{14}	19.78	1.97	0.88
LiCl	2.57_{15}	113	104	3.41^9	12.2^{14}	15.46	2.78	1.09
LiBr	2.74_5	183	190	4.31^9	14.0^{14}	14.49	3.04	1.20
LiI	3.00_0	363	470	6.2^{10}	16.7^{14}	13.25	3.56	1.30
NaF	2.30_{95}	46	31	2.11^{11}	9.8^{14}	17.22	2.13	1.03
NaCl	2.814	180	180	4.263^{12}	11.0^{14}	14.13	2.54	1.03
NaBr	2.98_1	271	300	5.08^9	11.9^{14}	13.34	2.71	1.11
NaI	3.23_1	482	630	7.0^{10}	13.5^{14}	12.31	2.97	1.16
KF	2.66_5	167	150	3.31^9	10.0^{14}	14.92	3.27	1.02
KCl	3.13_{85}	452	560	5.63^9	10.1^{14}	12.67	3.32	0.99
KBr	3.29_3	605	800	6.70^9	11.0^{14}	12.08	3.31	1.05
KI	3.52_6	924	1420	8.54^9	12.5^{14}	11.28	3.36	1.14
RbF	2.81_5	278	290	4.3^{10}	10.0^{10}	14.13	3.94	0.93
RbCl	3.27	691	960	6.9^{10}	9.85^{14}	12.16	3.97	0.89
RbBr	3.42_7	898	1340	7.94^9	10.4^{14}	11.60	3.89	0.94
RbI	3.66_{25}	1330	2240	9.58^9	11.9^{14}	10.86	3.87	1.09
CsF	3.00_4	495	600	4.6^{10}	10.0^{10}	12.23	4.77	1.06
CsCl	3.56_0	1530	2600	5.9^{13}	13.65^{15}	11.27	5.31	1.43
CsBr	3.71_3	2070	3600	7.0^{13}	13.9^{15}	10.80	5.54	1.40
CsI	3.95	2970	5800	9.3^{13}	14.6^{15}	10.15	5.48	1.33

10	11	12	13	14	15	16	17
τ $\times 10^{12}$ erg	$\delta=r_- - r_+$ $\times 10^8$ cm	$Se^{-(a-1)r_0/\rho}$	$(r_+ + r_-)$calc. (Eq. 12) $\times 10^8$ cm	$\delta(r_+ + r_-)$ $\times 10^8$ cm	r_0(calc.) (Eq. 13) $\times 10^8$ cm	$\delta(r_0)$ (Col. 2–Col. 15) $\times 10^8$ cm	$\delta(r_0)$ (Eq. 14) $\times 10^8$ cm
20.87	0.635	0.463	1.591	+0.006	2.002	+0.008	+0.008
17.16	1.000	.643	1.960	+ .010	2.557	+ .014	+ .014
16.33	1.125	.748	2.072	− .003	2.748	− .003	− .004
15.51	1.310	.939	2.243	− .017	3.020	− .020	− .023
18.32	0.235	.187	1.980	− .006	2.318	− .008	− .008
15.64	0.600	.216	2.353	+ .003	2.810	+ .004	+ .004
14.94	0.725	.248	2.475	.000	2.981	.000	.000
14.11	0.910	.309	2.661	+ .001	3.229	+ .002	+ .002
17.17	−0.075	.124	2.282	− .013	2.685	− .020	− .018
15.00	0.290	.074	2.668	+ .008	3.127	+ .012	+ .011
14.34	0.415	.076	2.790	+ .005	3.286	+ .007	+ .007
13.49	0.600	.092	2.973	+ .003	3.521	+ .005	+ .005
17.14	−0.210	.130	2.411	− .019	2.845	− .030	− .027
15.24	0.155	.055	2.797	+ .002	3.267	+ .003	+ .003
14.55	0.280	.052	2.923	+ .003	3.422	+ .005	+ .004
13.63	0.465	.056	3.112	+ .007	3.653	+ .010	+ .009
16.94	−0.345	.141	2.570	+ .004	2.996	+ .008	+ .005
15.15	0.020	.173	2.920	− .010	3.572	− .012	− .014
14.94	0.145	.161	3.057	+ .002	3.709	+ .004	+ .003
14.30	0.330	.179	3.252	+ .012	3.931	+ .019	+ .017
			Average	±0.007		±0.010	

[8] P. P. Ewald and C. Hermann, *Strukturbericht 1913–1928*, Akad. Verlagsgesellschaft, Leipzig, 1931.

[9] J. C. Slater, Phys. Rev. **23**, 488 (1924).

[10] Estimated.

[11] P. Bridgman, Proc. Am. Acad. **64**, 19 (1929).

[12] P. Bridgman, Proc. Am. Acad. **66**, 255 (1931).

[13] T. W. Richards and E. P. R. Saerens, J. Am. Chem. Soc. **46**, 934 (1924).

[14] F. A. Henglein, Zeits. f. Elektrochem. **31**, 424 (1925).

[15] G. P. Baxter and C. F. Hawkins, J. Am. Chem. Soc. **38**, 266 (1916).

with the assumed radii. The close agreement is indicated by the figures in Column 14 of Table II.

The degree of agreement is very sensitive to small changes in the differences between radii of ions of the same sign. Additions or subtractions of a rather large constant to each of the negative ion radii, accompanied by subtractions or additions of the same constant to each of the positive ion radii, with further adjustment of the Li^+ radius, can be made, however, without altering the agreement markedly. We cannot claim that the radii of Table I are the *best* values but they form a consistent set; moreover all sets giving agreement with the data must have practically the same *differences* between the individual negative ion radii, also nearly the same *differences* between the individual positive ion radii, excluding Li^+.

To recalculate r_0 from the assumed radii values of Table I, Eq. (12) is transformed to give Eq. (13).

$$r_0 - 4.606\rho \log_{10} r_0 = (r_+ + r_-) + 2.303\rho \log_{10}(bMc_{+-}/\rho) - 2.303\rho \log_{10}(r_0\tau) + 2.303\rho \log_{10}(1 + Se^{-(a-1)r_0/\rho}). \quad (13)$$

Small differences in r_0 change but slightly the last two terms (since the largest additive term of $r_0\tau$ is a constant, αe^2), hence by successive approximations values of r_0 (calc.) which satisfy the equation can be readily obtained. These are given in Column 15 of Table II. Comparison with the r_0 (exp.) values in Column 2 gives the differences in Column 16. These differences are practically within the probable error of the experimental r_0 values, hence we can consider our assumptions of an exponential repulsive potential, with constant radii and a single constant ρ to be well substantiated.

An alternative method for the calculation of these differences is by means of the following approximate equation:

$$\delta(r_0) = \delta(r_+ + r_-) \cdot (\sigma N\beta/9V) \approx 1.4\delta(r_+ + r_-). \quad (14)$$

Values of $\delta(r_+ + r_-)$ may be taken from Column 14 of Table II; σ is defined by the equation

$$\sigma = r_0^2(\partial^2 B(r)/\partial r^2). \quad (15)$$

Its values have been calculated for the alkali halides by Born and Mayer.[3] For all of them the value of the fraction $(\sigma N\beta/9V)$ is approximately 1.4. As may be seen from a comparison of Columns 16 and 17, the use of Eq. (14) with this constant value 1.4 introduces no errors greater than 0.003A for these salts, the average error being less than 0.001A.

In the calculation of the quantities given in Table II the figures were all carried to at least one more decimal place than there indicated so that the deviations of the $\delta(r_+ + r_-)$ values (Column 14) from zero and of the $\delta(r_0)$ values (Columns 16 and 17) from each other are not due to inaccuracies in the arithmetical computations.

Comparison of the resuits of the individual determinations of r_0, as given in the *Strukturbericht*, with the r_0 (calc.) values shows that the latter agree with the experimental values well within the accuracy of the average experimental determination but not within the probable accuracy of the best determinations. Slight changes in the assumed radii might better the agreement somewhat but not a great deal.

It should be noted that the deviations from additivity of interatomic distances due to differences in sizes of the ions amount to as much as 0.14A and deviations from additivity due to difference in structure type amount to as much as 0.10A.

The Lattice Energies of the Cuprous Halides

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Following exactly the method employed in the case of the silver halides the lattice energies of the cuprous halides have been calculated. The exponential constant in the empirical repulsion equation expressing the positive repulsive potential between the ions is found to be almost the same as that for the silver halides. The energies of the salts indicate that, particularly for the iodide there is not purely ionic binding. The lattice energies are calculated to be, for CuCl 216 kcal., CuBr, 208 kcal., CuI 199 kcal. The "experimental" values are, CuCl 221.9 kcal. CuBr 216.0 kcal. and CuI 213.4 kcal.

INTRODUCTION

RECENTLY calculations have been made of the lattice energies of the alkali halides[1] and of the silver and thallous halides[2] following a method proposed by Born and Mayer.[3] In this paper the arithmetical calculations are carried out for the cuprous halides.

The method is exactly the same as that used for the silver halides, and the Table I of this paper follows exactly the contents of Tables I, II, and III of the previous article.[2]

The compressibilities are taken from an article by Bridgman.[4] The frequencies assumed for the negative ions are those assumed for the silver salts. The polarizability of the cuprous ion is taken from Pauling.[5] The experimental lattice constants assumed are those of the *Strukturbericht*.[6] The energies of reaction are all taken from *International Critical Tables*, with the exception of the heat of sublimation of copper, which is estimated from the boiling point with the aid of Hildebrand's modification of Trouton's rule. The electron affinity of the halides are taken from the calculations on the alkali halides.[1]

The disagreement of 2.9, 5.0, and 11.4 kcal. for the chloride, bromide, and iodide, respectively, between the theoretical lattice energies and the "experimental" values, may in part be due to an uncertainty in the heat of sublimation of copper; however, it is more probable that they

TABLE I.

		CuCl	CuBr	CuI
1	Salt			
2	Crystal type	Zincblend	Zincblend	Zincblend
3	Q_{00}^2 (neg. ion) $\times 10^{16}$ cm^2	3.40	4.08	5.27
4	ϵ (neg. ion) $\times 10^{12}$ ergs/molecule	15.6	13.9	11.0
5	α (neg. ion) $\times 10^{24}$ cm^3	3.45	4.47	7.29
6	α (pos. ion) $\times 10^{24}$ cm^3	0.43	0.43	0.43
7	ϵ (pos. ion) $\times 10^{12}$ ergs/molecule	29	29	29
8	$c_{++} \times 10^{60}$ ergs $\times$cm^6	0.41	0.41	0.41
9	$c_{--} \times 10^{60}$ " "	133	208	437
10	$c_{+-} \times 10^{60}$ " "	21.9	27.3	37.7
11	$d_{++} \times 10^{76}$ ergs $\times$cm^6	0.2	0.2	0.2
12	$d_{--} \times 10^{76}$ " "	270	470	1230
13	$d_{+-} \times 10^{76}$ " "	27	38	64
14	S_0'	4.354	4.354	4.354
15	S_0''	0.762	0.762	0.762
16	S_b'	4.104	4.104	4.104
17	S_b''	0.253	0.253	0.253
18	$C \times 10^{60}$ ergs $\times$cm^6	146	198	330
19	$D \times 10^{76}$ ergs $\times$cm^8	150	220	420
20	$r_0 \times 10^8$ cm	2.34	2.46	2.62
21	$\beta \times 10^6$ (compressibility) bars^{-1}	2.51	2.93	2.81
22	$V^{-1}(\partial V/\partial T)_p \times 10^6$	65.4	62.1	73.5
23	$9V/N\beta \times 10^{13}$ ergs/molecule	142	141	177.5
24	$(3T/N\beta)(\partial V/\partial T)_p \times 10^{12}$ ergs/molecule	0.94	0.88	1.32
25	$\alpha\epsilon^2/r_0 \times 10^{12}$ ergs/molecule	15.97	15.20	14.26
26	$C/r_0^6 \times 10^{12}$ ergs/molecule	0.89	0.89	1.01
27	$D/r_0^8 \times 10^{12}$ " / "	0.16	0.16	0.19
28	τ $\times 10^{12}$ " / "	21.67	20.97	20.51
29	σ $\times 10^{12}$ " / "	223	220	262
30	σ/τ	10.3	10.5	12.8
31	$\rho \times 10^8$ cm (average value $=0.223$)	0.227	0.235	0.205
32	r_0/ρ calculated from average	10.51	11.07	11.76
33	$B(r) \times 10^{12}$ ergs/molecule	2.05	1.88	1.72
34	$\frac{1}{2}h\nu \times 10^{12}$ " / "	0.08	0.06	0.05
35	$U \times 10^{12}$ " / "	14.89	14.32	13.69
36	U (theoretical lattice energy) kcal.	216	208	199
37	$MX_{cr.}$ 0°K$\rightarrow MX_{cr.}$ 291°K, ΔH kcal.	2.8	2.9	3.0
38	$MX_{cr.} \rightarrow M_{g.s.} + \frac{1}{2}X_{2\,g.s.}$ 291°K, ΔH kcal.	32.5	24.6	15.8
39	$\frac{1}{2}X_{2\,g.s.} \rightarrow X_g$ 291°K ΔH kcal.	28.8	26.7	25.5
40	X_g 291°K $\rightarrow X_g$ 0°K " "	-1.1	-1.1	-1.1
41	$X_g + e^- \rightarrow X_g^-$ 0°K " "	-86.5	-81.5	-74.2
42	$M_{cr.}$ 291°K$\rightarrow M_{cr.}$ 0°K " "	-1.7	-1.7	-1.7
43	$M_{cr.}$ 0°K$\rightarrow M_g$ 0°K " "	70.0	70.0	70.0
44	M_g 0°K$\rightarrow M_g^+ + e^-$ 0°K " "	177.0	177.0	177.0
45	Sum $MX_{cr.} \rightarrow M_g^+ + X_g^-$ 0°K (lattice energy) ΔH kcal.	221.9	216.0	213.4
46	Difference 36 and 45 $\delta\Delta H$ kcal.	2.9	5.0	11.4
47	Assumed value b_-	77.4	105.3	189.5
48	" " b_+	202	202	202
49	Calculated $r_0 \times 10^8$ cm	2.34	2.49	2.59
50	Experimental $r_0 \times 10^8$ cm	2.34	2.46	2.62
51	Difference $\delta r \times 10^8$ cm	+0.002	−0.03	+0.03

[1] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 16 (1932).

[2] J. E. Mayer, J. Chem. Phys. **1**, 327 (1933).

[3] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

[4] P. W. Bridgman, Proc. Am. Acad. Arts and Sci. **67**, 345 (1932).

[5] L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).

[6] P. P. Ewald and C. Hermann, *Strukturbericht*, 1913–1928.

show a considerable homopolar binding component. The calculated lattice constants (row 49) show irregular disagreement with the experimental values. This may in part be due to uncertainty in the experimental values but again is probably caused by an error in the assumptions. Table II, however, shows that the purely ionic crystal should be stable in crystal type in which these salts do crystallize, the Zincblend lattice.

Reliable evidence as to whether these crystals are in reality considerably homopolar or very nearly purely ionic can probably only be obtained by a theoretical calculation of the ionic non-electrostatic (Heitler-London) repulsion from ionic electron wave functions.

TABLE II. *Calculation of the potential energy change with lattice type.*

energies in 10^{-12} ergs/molecule

Salt	Experimentally stable lattice	Hypothetical lattice	Change at constant r_0 of						
			$-\frac{\alpha_e^2}{r_0}$	$-\frac{C}{r_0^6}$	$-\frac{D}{r_0^8}$	$B(r_0)$	$\frac{\partial^2\Phi}{\partial r^2}\frac{(\delta r)^2}{2}$	$\delta\Phi$
CuCl	Zincblend	Rocksalt	−1.07	−0.73	−0.13	+2.32	−0.13	+0.24
CuBr	Zincblend	Rocksalt	−1.02	−0.76	−0.14	+2.38	−0.13	+0.33
CuI	Zincblend	Rocksalt	−0.95	−0.95	−0.18	+3.36	−0.13	+0.14

On the Binding Forces in the Alkali and Alkaline Earth Metals According to the Free Electron Theory

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Although there have been a considerable number of attempts to work out in some detail the nature of the cohesive forces in the alkali metals, it has seemed worth while to see how far one could go with the simplest possible hypothesis, according to which the metal consists simply of singly charged positive ions in a sea of free electrons. Frenkel first showed that the fact that the electrons obey the Fermi statistics, results in an effective repulsive force which will be balanced by attractive electrical forces; but, as he pointed out, the finite size of the ions prevents this being more than a qualitative picture, and he suggested taking this into account by including repulsive forces between electrons and ions. In the present work an intrinsic ionic volume has been introduced into which the electrons are supposed to be unable to penetrate; this is simply subtracted from the atomic volume in the Fermi expression for the kinetic energy of the electrons. For the attractive potential an expression like those commonly employed to get the electrical potential of crystals is used; it involves a "Madelung constant" of a size about equal to those occurring in cases of uni-univalent crystals, and the same for all the alkali metals. For the alkaline earth metals appropriate modifications can be made. One can then calculate the energy of the metals from the experimental value of the atomic volume, getting excellent agreement with experiment in the case of the alkali metals, but not such good agreement in the case of the alkaline earth metals. The method appears not to be very successful in calculating the compressibilities, even in the case of the alkali metals (for which, alone, it was tried); but aside from the fact that the compressibilities at absolute zero may only be inferred from measurements around room temperature, it appears that a relatively small correction to the energy expression can give the correct compressibility without greatly upsetting the calculation of the energy. The latter then is to be considered as of significance, and gives some confidence in the essential correctness of the simple picture of the metal described above.

§1. The Energy of an Alkali or Alkaline Earth Metal

ACCORDING to the simplest possible picture of a metal, it should consist simply of a number of positive ions immersed in a Fermi electron gas. Such a picture is, indeed, capable of explaining and correlating many of the electric and magnetic properties of metals. If it comes anywhere near being a correct representation of the facts, it should also be capable of explaining the binding properties of at least the "most metallic" metals, such as the alkali and alkaline earth metals. A number of attempts have been made to study these binding properties on the basis of more elaborate theories.[1] All these investigations are valuable in throwing light on the nature of the forces operating in metals, but do not lessen the interest in seeing how far the most simple hypotheses will carry us.

The first consideration of the binding properties from this point of view is due to Frenkel.[2] He pointed out that the fact that the electrons obey the Fermi statistics results in what is effectively a repulsive force, which is balanced by the attractive force between the electrons and positive ions, much as the repulsive forces between ions of crystals are balanced by the electrical attraction between the positive and negative ions.

The mathematical formulation of these statements is as follows. In a univalent metal (at the absolute zero of temperature) the average kinetic energy per electron, due to the fact that in the Fermi statistics only two electrons can occupy

[1] See, e.g., Slater, Phys. Rev. **35**, 509 (1930); Taylor, Eyring and Sherman, J. Chem. Phys. **1**, 68 (1933); Wigner and Seitz, paper presented at the Washington meeting of the American Physical Society, April 28, 1933, Phys. Rev. **43**, 1048 (1933). (Just after this paper was submitted their article, Phys. Rev. **43**, 804 (1933) was received.)

[2] Frenkel, Zeits. f. Physik **49**, 31 (1928) especially p. 42; *Wave Mechanics, Elementary Theory*, Oxford University Press, 1932, p. 221 ff.

the same quantum state, is given by the expression

$$\epsilon = \tfrac{3}{5}(3/4\pi GV)^{\frac{2}{3}} h^2/2m = p/V^{\frac{2}{3}}, \quad (1)$$

where $G=2$ is the number of electrons which simultaneously may be in a given quantum state, V is the atomic volume, this being equal to the volume occupied by an electron in a univalent metal, h is Planck's constant, m the mass of an electron, and p is defined by the equation. The potential due to the electrical forces may be written in the form

$$U = -e^2 A V^{-\frac{1}{3}}, \quad (2)$$

where e is the charge on the electron and A is a constant, which may be described as the Madelung constant for the metal.

The total energy of the metal per atom at absolute zero is then given by

$$E = \epsilon + U. \quad (3)$$

At equilibrium at absolute zero

$$dE/dV = 0. \quad (4)$$

This puts a condition on V_e, the equilibrium value of V, from which it may be calculated. As Frenkel noted this will give the same value of V_e for all the alkali metals. That this conclusion is not confirmed by the facts, is due, as he pointed out, to the finite size of the ions, and he attempted to correct for it by introducing non-electrostatic repulsive forces between the electrons and ions. On account of the difficulty of evaluating the constants involved, however, no numerical calculations were made.

If, however, in place of introducing these non-electrostatic forces in the form used by Frenkel, we simply correct[3] V in (1) by an amount V_i, which we may call the intrinsic ionic volume, we get in place of (1)

$$\epsilon = p(V - V_i)^{-\frac{2}{3}} \quad (5)$$

and (3) becomes

$$E = p(V - V_i)^{-\frac{2}{3}} - e^2 A V^{-\frac{1}{3}}. \quad (6)$$

This assumes that the expression (2) is not altered by the fact that the ions occupy a finite volume. This cannot be strictly true, but is probably a reasonably good approximation as the forces between the ions and electrons depend largely on the average positions of the electrons; in any event (2) should not be as strongly affected by the finite volume of the ions as (1). Differentiation of (6) gives us

$$-\tfrac{2}{3}p(V_e - V_i)^{-5/3} + \tfrac{1}{3}e^2 A V_e^{-4/3} = 0, \quad (7)$$

which provides a means of calculating V_i if V_e is known. If we solve for $V_e - V_i$ and put it in (6) we get for E_e, the equilibrium value of E,

$$E_e = pV_e^{-8/15}(e^2 A/2p)^{2/5} - e^2 A V_e^{-\frac{1}{3}}. \quad (8)$$

It is seen that Eq. (8) provides us with a relation between the atomic volume, V_e, and the total energy of the metal, E_e. The latter quantity is the energy which is necessary to completely decom-

[3] After I had worked out the consequences of these assumptions, Professor J. C. Slater told me that he had previously attempted a somewhat similar correction. He did not publish any results, because of the difficulty of explaining the compressibilities and the heats of sublimation of the various metals at the same time. I believe, however, that I have shown later in the paper that this difficulty is only an apparent one. I am very much indebted to Professors Slater and Kemble and others of the group in Cambridge for helpful discussions of this work.

More recently I have had the opportunity of discussing the paper with Dr. Irving Langmuir. From him I learned that he, also, had previously made some calculations of a similar nature (though differing somewhat in details) which remain as yet unpublished.

The question as to the exact physical cause of the existence of the intrinsic ionic volume is one about which it seems best not to make any definite statement at present. It has been suggested that it is due to the fact that the only way that a valence electron can get into the region near the nucleus of one of the positive ions is by being a penetrating electron, but such an electron (to speak in terms of the old quantum theory) can, on account of its high velocity while there, spend but a relatively short time in the neighborhood of the nucleus, and this region therefore acts to some extent like a region into which it cannot go. In addition to this, the electron may tend to get "promoted" out of such a penetrating orbit, and thus not go into the neighborhood of the positive nuclei at all, for such promotion, though requiring energy when the atoms are isolated, may actually result in a lowering of energy in the fairly closely packed metallic structure.

It may be well to mention at this point another repulsive potential which comes in, namely, the Heitler-London type repulsion of ions. On account of the large distances between the ions this contributes negligibly to the energy of the system, as is shown by a calculation very kindly sent to me by Dr. J. E. Mayer.

pose the crystal into gaseous ions and electrons at absolute zero. If we subtract from it the energy of ionization of the gaseous atom, we have a value of the energy of sublimation at absolute zero. Eq. (8) thus gives us the possibility of calculating the energy of sublimation from the experimental value of V_e; the result may then be compared with the experimental value of the energy of sublimation, and this comparison should give us some further information as to the validity of the simple electron-gas theory of metals.

In the case of a bivalent metal, if we continue to define V as the atomic volume, and V_i as the intrinsic volume of one ion, the volume $V-V_i$ is occupied by two electrons. This introduces the factor $2^{\frac{2}{3}}$ into the expression for ϵ, Eq. (5). Further, since there are two electrons per atom, if ϵ is to remain the energy per atom, we must introduce another factor of 2. Thus, if, for bivalent metals, we redefine p as $2^{5/3}$ times its former value, and introduce an appropriate new value for the Madelung constant A, we can repeat the argument which led to Eq. (8). Hence with the new values of p and A the latter equation may be taken as applying also to bivalent metals.

In order to apply Eq. (8) to calculate the energy of the metal, it is necessary, as we have mentioned, to use an experimental value of V_e. For the alkali metals, I have used the estimates made by Simon and Vohsen[4] of the atomic volumes at the absolute zero of temperature. For the alkaline earth metals I have simply used the densities calculated from the crystal structure data given by Wyckoff.[5] These data are presumably for room temperature, but since these elements are rather high melting the values should deviate but a very few percent from the values at absolute zero; furthermore, the error thus made should be about the same for all the alkaline earths.

It is also necessary to make some estimate of the value of A. Sherman,[6] in a recent review, has tabulated the values of the Madelung constant for a number of different crystal structures. For various uni-univalent crystals, which resemble univalent metals, it ranges from about 2.0 to 2.4, while for uni-bivalent crystals which are like bivalent metals it ranges from about 6.5 to 8.0. We have chosen the value 2.08 for the alkali metals, and the value 6.6 for the alkaline earths.

In Table I we have given the results of the application of Eq. (8). The second column gives the value of V_e, and in succeeding columns we have given[7] ϵ_e, U_e and E_e. Finally we have tabulated the ionization potential[8a] (I) and obtained the heat of sublimation (H_s) and compared the latter with the experimental values,[8b] which are tabulated in the last column. It will be seen that the agreement between the calculated and experimental values is very good in the case of the alkali metals, and this is especially notable when we consider that the calculated value of H_s is a rather small difference between two large quantities.[9]

TABLE I. *Calculation of the energy of sublimation.* (All energies in volt-electrons)

Metal	V_e(A^3)	ϵ_e	$-U_e$	$-E_e$	I	H_s (calc.)	H_s (expt.)*
Li	20.71	3.704	10.831	7.127	5.368	1.76	1.66
Na	37.60	2.695	8.878	6.183	5.116	1.07	1.13
K	71.6	1.912	7.164	5.252	4.321	0.93	0.94
Rb	87.6	1.717	6.698	4.981	4.159	0.82	0.865
Cs	108.7	1.530	6.232	4.702	3.877	0.825	0.83
Mg	23.5	11.00	32.96	21.96	22.58	−0.62	1.58
Ca	43.0	7.97	26.95	18.98	17.91	1.07	2.06
Sr	55.4	6.96	24.76	17.80	16.65	1.15	1.72
Ba	62.9	6.50	23.73	17.23	15.14	2.09	2.13

* These values are for room temperature, but differ very little from the values for absolute zero.

It may be argued that the good agreement is conditional upon the choice of A, in which we are allowed some latitude. This is of course true, but aside from the intrinsic reasonableness of the values of A chosen, we may note that we

[4] Simon and Vohsen, Zeits. f. physik. Chemie **133**, 165 (1928).

[5] Wyckoff, *The Structure of Crystals*, 2nd edition, Chemical Catalog Co., 1931, p. 204.

[6] Sherman, Chem. Rev. **11**, 95 (1932). Table on p. 107. Our A corresponds to Sherman's A_{δ_0}.

[7] Frenkel, Zeits. f. Physik **50**, 234 (1928), has shown that for a system in which all the forces are electrical the kinetic energy will be minus twice the potential energy. In this case, this amounts practically to $|\epsilon| = \frac{1}{2}|U|$. It will be observed that this is not the case in Table I. This is presumably because the introduction of an intrinsic ionic volume implies forces which for our purposes are not electrical forces.

[8] (a) Sherman, reference 6, p. 138; (b) ibid., p. 136.

[9] The following values of V_i/V_e, obtained in the calculation, may be of interest: Li, 0.315; Na, 0.419; K, 0.465; Rb, 0.487; Cs, 0.509.

have used the same value for all the alkali metals, which lends added significance to our calculations, as we see that we reproduce very well the trends in the value of H_s.

In the case of the alkaline earth metals the agreement is by no means so satisfactory, though even here the percentage error in E_e is not large. We have chosen the rather low value of 6.6 for A in order to get good agreement with barium. Of all the alkaline earth metals, barium is the one to which a simple free electron theory would be expected to be the most applicable. With this value of A it is seen that the experimental values show a marked trend away from the theoretical in the case of the alkaline earths, and in every case the experimental value of the heat of sublimation is larger. This is perhaps to be expected, since it implies a lower energy for the metal than we have calculated; if the values of the constants we have used are correct and the theory right as far as it goes, but our results are incorrect through neglect of some factor which ought to be taken into account, we should expect the deviation to be in this direction, since the actual metal will tend to seek the lowest possible energy level. On the other hand, there remains the possibility that the Madelung constant will vary more from metal to metal in the case of the alkaline earths than in the case of the alkalis because of the effect of the more complicated repulsions and attractions on the distribution of the electrons of the former.

§2. The Compressibility

It should be possible, from the second derivative of E, to get the value of the compressibility at the absolute zero of temperature. We have the general thermodynamic equation

$$P = T(\partial P/\partial T)_V - (\partial E/\partial V)_T, \tag{9}$$

where P is the external pressure and T is the temperature. From this we see

$$(\partial P/\partial V)_T = T(\partial^2 P/\partial V \partial T) - (\partial^2 E/\partial V^2)_T. \tag{10}$$

At $T=0$ the first term on the right drops out, and we may write for the compressibility at equilibrium ($P=0$), which is defined as $\kappa_e = -V_e^{-1}(\partial V/\partial P_e)_T$ the well-known relationship

$$\kappa_e = V_e^{-1}[(\partial^2 E/\partial V_e^2)_T]^{-1}. \tag{11}$$

Differentiating (6) twice and using the relation (7) we find

$$\left(\frac{\partial^2 E}{\partial V_e^2}\right)_T = \frac{10}{9} p\left(\frac{e^2 A}{2p}\right)^{8/5} V_e^{-32/15} - \frac{4}{9} e^2 A V_e^{-7/3}, \tag{12}$$

which may be used in (11) to give the compressibility. It is, however, more satisfactory to compare the theoretical and experimental values of $(\partial^2 E/\partial V_e^2)_T$ and this has been done in Table II.

Table II. *Calculation of* $\partial^2 E/\partial V_e^2$.

(All energies in ergs and volumes in cm³—all quantities to be multiplied by 10^{33})

Metal	$\partial^2\epsilon/\partial V_e^2$	$-\partial^2 U/\partial V_e^2$	$\partial^2 E/\partial V_e^2$ (calc.)	$\partial^2 E/\partial V_e^2$ (expt.)
Li	32.6	17.8	14.8	5.8
Na	9.14	4.44	4.70	1.9
K	2.32	0.99	1.33	0.53
Rb	1.51	0.62	0.89	0.17
Cs	0.95	0.37	0.58	0.065

The experimental values of $(\partial^2 E/\partial V_e^2)_T$ have been computed from the data of Bridgman[10] by the use of Eq. (10). A word as to how this was done will perhaps not be out of place. The method Bridgman uses to present his data is to give $\Delta V/V_0$ as a function of P, the applied pressure. Here ΔV is the change of volume when the substance is compressed from zero pressure to pressure P, and V_0 is some standard volume, usually the volume of the substance at zero pressure and room temperature. ΔV, however, is not the difference between the actual volume of the metal, at pressure P and temperature T, and V_0, but it is the difference between the volume at pressure P and the volume at zero pressure and the same temperature. Bridgman's method of presenting the data is not, however, the most convenient for our purposes, and in Figs. 1 and 2, I have plotted $V_0(\partial P/\partial V)_T$ as a function of $\Delta' V/V_0$. My $\Delta' V$ differs from Bridgman's ΔV in that I have corrected for the thermal expansion where data for more than one temperature is given. Thus, in all cases $\Delta' V$ is the same as ΔV for the lower temperature. For the higher temperature, however, $\Delta' V$ is the difference between the actual volume at the given pressure and temperature and the volume at zero pressure and the lower temperature. (The latter volume may for our purposes be taken as equal to V_0). In this way, the differences in the ordinates of the curves give one directly $V_0(\partial^2 P/\partial V \partial T)$, whence we may get $V_0(\partial^2 E/\partial V^2)_T$ from (10).

In the case of lithium Bridgman gives $\Delta V/V_0$ as a function of P for 30 and 75°C by means of formulas. From these formulas and their derivatives all necessary information is readily obtained. In the case of sodium

[10] Bridgman, Proc. Am. Acad. **58**, 202 (1923); **60**, 399, 409 (1925).

$\Delta V/V_0$ was given as a function of P for 30 and 75° by means of tables. Approximate values of $V_0(\partial P/\partial V)_T$ were obtained simply by taking differences of $\Delta V/V_0$ over a pressure interval, and dividing into the difference in pressure. These were used as the ordinates for the figure and the mean values of $\Delta V/V_0$ over the intervals were used as the corresponding abscissas. This will give a curve which is very approximately correct. In the case of potassium, data were given in the form of a table, but for 45° only. However the thermal expansion was given as a function of the pressure, and, similarly, in the cases of rubidium and caesium data for only one temperature, 50°C, were given, but it was stated that the thermal expansion was independent of pressure up to 8000 or 9000 kilograms per cm. This enables one to get $\partial^2 P/\partial T\partial V$ in the following way:

$$(\partial P/\partial T)_V = -(\partial P/\partial V)_T(\partial V/\partial T)_P.$$

Hence

$$\partial^2 P/\partial T\partial V = -(\partial^2 P/\partial V^2)_T(\partial V/\partial T)_P - (\partial P/\partial V)_T[\partial(\partial V/\partial T)_P/\partial V].$$

The second term on the right-hand side of the last expression drops out for rubidium and caesium, since the thermal expansion is independent of pressure (hence of volume) in the low part of the pressure range, and can be evaluated from the data given for potassium. The first term can also be evaluated in terms of the data given and the thermal expansion. In this way I have obtained sufficient material to calculate $(\partial^2 E/\partial V^2)_T$ for potassium, rubidium, and caesium, and I have given in Table II the value obtained for 45° or 50°C and that particular pressure at which, as nearly as may be judged from the density data,[11] the substances have the same atomic volume as at absolute zero and zero pressure. In all cases I have plotted the values of $V_0(\partial^2 E/\partial V^2)_T$ as a function of $\Delta' V/V_0$ in Figs. 1 and 2 (dotted curves). In each case the value given in Table II is the value for the mean of the temperatures for which curves are drawn and at such a pressure that the substance has an atomic volume equal to that at absolute zero and zero pressure.

It is seen from Table II that there is a considerable discrepancy[12] between the calculated and experimental values of $(\partial^2 E/\partial V_e^2)_T$. One is tempted to ask whether this discrepancy would still exist, if one could evaluate $(\partial^2 E/\partial V_e^2)_T$ at the absolute zero. It is impossible to answer this question at present, but we may make the following observations. From the calculated values of $(\partial^2 E/\partial V_e^2)_T$ (neglecting the effect of the higher derivatives) it appears that the energy necessary to compress the metal (if it behaved as it should according to the calculation) to 95 percent of V_e would in all cases be around 0.005 volt; to compress it to 90 percent of V_e would require around 0.02 volt. This will give some idea of the amount of energy due to thermal agitation which would have to be "squeezed out" on compression at room temperatures, if that is the cause of the deviation of the experimental value of $(\partial^2 E/\partial V_e^2)_T$ from that calculated for absolute zero. As the value of kT for $T = 300°$ abs. is around 0.026 volt these amounts of energy seem a little large, but not, perhaps, entirely beyond reason. In any event, it is obvious, simply by looking at the curves in Figs. 1 and 2, that

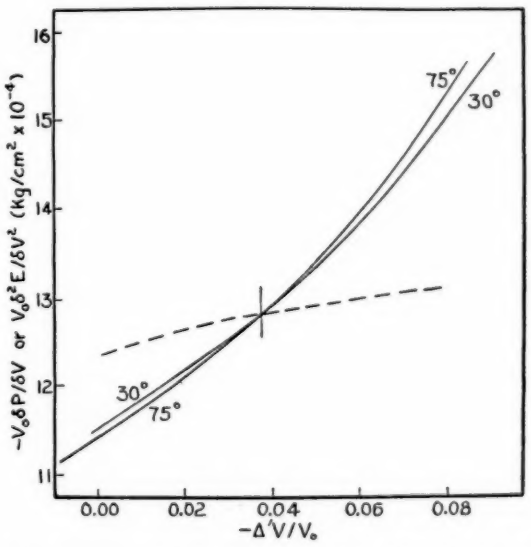

FIG. 1. $V_0\partial P/\partial V$ (solid lines) and $V_0\partial^2 E/\partial V^2$ (broken line) for Li. Vertical line indicates volume at 0°K.

[11] Landolt-Börnstein Tabellen. The "mean values" of the densities, listed at the side of the tables, were those used.

[12] Professor Slater has pointed out to me that this discrepancy is in the direction to be expected. For if we gradually separate the atoms of a metal and let the electrons go where they will, they will not be uniformly distributed through the space allotted to them, but each one will tend to attach itself to an atom. We thus do not finally arrive at a state of ions and free electrons, but we have instead simply separated atoms. The energy involved in this process is just the energy of sublimation, which is a much smaller quantity than E. If this process is already starting in the actual metal we should expect the minimum of the potential curve to be flattened out, and hence $(\partial^2 E/\partial V_e^2)_T$ will be smaller than calculated. There is nothing in the correction made below which is inconsistent with this view of the behavior of the metal. The Heitler-London type repulsion mentioned[3] will, if taken into account, tend to increase the discrepancy in the compressibilities, but this is presumably not as important as the effect just considered.

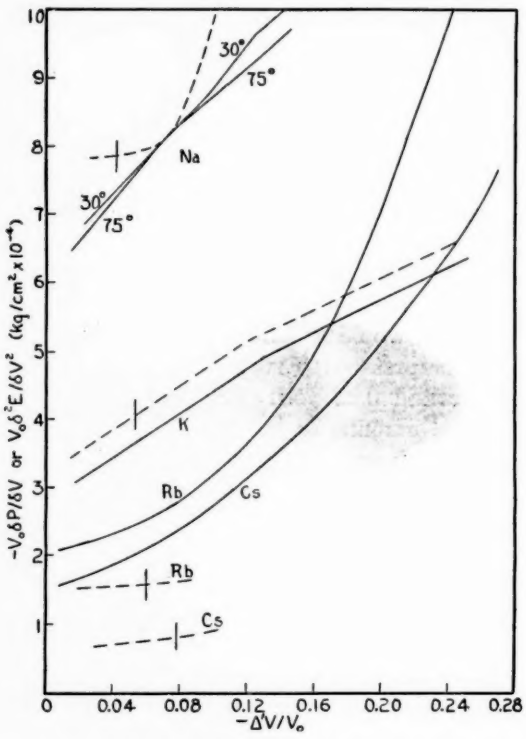

FIG. 2. $V_0\partial P/\partial V$ (solid lines) and $V_0\partial^2E/\partial V^2$ (broken lines) for the alkali metals except Li. Vertical lines indicate volumes at 0°K.

some theory which neglects fewer things than the present one will be necessary to account for their behavior at a single temperature, and one is tempted to think that this peculiar behavior may have something to do with the thermal motion. This feeling is strengthened by the following considerations. It is possible, from the data given by Bridgman, to calculate $(\partial P/\partial T)_V$ from the relation $(\partial P/\partial T)_V = -(\partial P/\partial V)_T(\partial V/\partial T)_P$. Thus we can evaluate $(\partial E/\partial V)_T$ from (9) and find the value of $\Delta V/V_0$ at which it is zero. This can be compared with the value of $\Delta V/V_0$ which gives a volume, at the temperature considered, equal to the equilibrium volume at absolute zero. This is done in Table III, and it is seen that in general the two values of $\Delta V/V_0$ are not equal. The

TABLE III. *Comparison of volume for which $\partial E/\partial V=0$ and volume at absolute zero.*

	Li (30°C)	Na (30°C)	K (45°C)	Rb (50°C)	Cs (50°C)
$-\Delta V/V_0$ for $\partial E/\partial V=0$	0.049	0.062	0.053	0.12	0.145
$-\Delta V/V_0$, absolute zero	0.038	0.042	0.053	0.06	0.08

difference may be due to experimental error in the densities and in the compressibility measurements, in the cases of lithium and sodium, but it hardly seems possible that this can account for the very large differences in the cases of rubidium and caesium. These considerations lead us to believe that the deviation between the experimental and theoretical values of $(\partial^2E/\partial V_e^2)_T$ might well be reduced if we had the correct experimental value for absolute zero, but we cannot draw any definite conclusion.

If we suppose that a considerable discrepancy will still persist at absolute zero, we may then ask whether the calculation of the energy of sublimation retains any significance, considering that its logical extension leads to results not in accord with the facts. Undoubtedly such lack of agreement, assuming, as really seems probable, that some of it at least still persists at absolute zero, is due to the crudity of the picture of the metal we have employed. Nevertheless, it seems entirely possible that such a picture will be of value in determining the energy of the metal, and yet will not be sufficiently exact when we attempt to determine the compressibility, since these two properties will not necessarily be equally sensitive to the errors which may be involved in our approximations.

It will therefore be of interest to see if a modification can be introduced into our expressions which will correct the discrepancy between the observed and calculated values of $(\partial^2E/\partial V_e^2)_T$ without upsetting the calculation of E_e. To this end we shall make a purely formal modification in U, without attempting to attach any physical significance to it. We write for U, instead of the expression (2), the expression

$$U=-e^2AV^{-\frac{1}{3}}[1+\alpha V_e^{-1}(V-V_e)], \quad (13)$$

α being the constant coefficient of what may be called a first order correction term. When $V=V_e$, it will be seen that U has its original form (though we may wish to change the value of A slightly) but the equilibrium condition $(\partial E/\partial V_e)_T=0$ now yields a slightly different value of V_e-V_i. We now have, instead of (7)

$$-\tfrac{2}{3}p(V_e-V_i)^{-5/3}+\tfrac{1}{3}e^2AV_e^{-4/3}(1-3\alpha)=0, \quad (14)$$

which gives us in place of (8)

$$E_e = pV_e^{-8/15}(e^2A/2p)^{2/5}(1-3\alpha)^{2/5} - e^2AV_e^{-1/3} \quad (15)$$

and in place of (12)

$$\left(\frac{\partial^2 E}{\partial V_e^2}\right)_T = \frac{10}{9}p\left(\frac{e^2A}{2p}\right)^{8/5} V^{-32/15}(1-3\alpha)^{8/5} - (4/9)e^2AV_e^{-7/3}(1-(3/2)\alpha). \quad (16)$$

Now if we give α the reasonably small value, 1/6 to 1/14 depending on the metal, we will cure the discrepancies in $(\partial^2 E/\partial V_e^2)_T$, even the very large ones in rubidium and caesium. But such a value of α will increase the value of E_e by amounts varying from 0.2 to 0.35 volt. This change can be met by lowering the value of A by about 4 percent. While this brings A down to about the lower limit for uni-univalent salts, the value is still quite reasonable, and still with the same value of A for all the alkalis and a suitable value of α we can fit both the energies of sublimation (within about ± 0.12 volt) and the compressibilities. While, as stated above, no special significance is to be attached to the particular form of correction used, it gives us some confidence in the essential correctness of the picture of the metal as composed of a series of singly-charged positive ions in a sea of free electrons, and seems to justify to a considerable extent the idealizations we have made in calculating the heat of sublimation. It must be admitted that corrections can be introduced in a form which is not as favorable to this thesis as the particular one we have used. I believe, however, that the essential point is that U is given pretty well by the expression (2) and that the approximate forms of U and ϵ then suffice to use in the equilibrium condition (4) to obtain a value of $V_e - V_i$ which can be substituted back into the term ϵ, which is relatively unimportant in E; while, on the other hand, $\partial^2\epsilon/\partial V^2$ is the most important term in $(\partial^2 E/\partial V^2)_T$ and the value of $V_e - V_i$ obtained from the equilibrium condition then becomes of more importance. It might perhaps be more logical, since we admit that some modification of the expression (2) is needed, to also admit that A may vary slightly from one metal to another and compare the experimental and calculated values of E rather than those of H_s. Perhaps we may best state, as our conclusion, simply that the experimental and calculated values of E agree well within the differences which might be expected to occur due to differences in the value of A. This conclusion is still a significant one, for the actual variation in E from one metal to another is much greater than could be expected simply from differences in A.

A New Method of Studying the Electrical Properties of Monomolecular Films on Liquids

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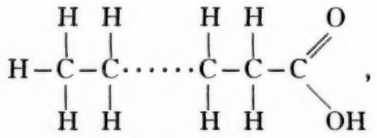
(Received May 29, 1933)

A new method of studying the electrical properties of monomolecular films floating upon a liquid has been described. Measurements on the potential jump, dV, because of the presence of monomolecular films of oleic acid, palmitic acid, tricaprylin, and trimyristin on water have been made in order to furnish a comparison with the work of Guyot. Excellent agreement was found in all cases. In addition, Guyot's conclusion was verified that dV for fatty acids depends greatly upon the presence of a trace of sulphuric acid in the water while dV for substances like tricaprylin and trimyristin is but slightly affected by the presence of acid.

I. NATURE OF OIL FILMS ON WATER

WHEN a drop of oleic acid or of any one of a large number of insoluble oils is placed on the surface of water, it rapidly spreads out into an invisible film. The early work of Devaux[1] and Pockels[2] demonstrated the existence of these films, while Lord Rayleigh pointed out the likelihood of their being but one molecule thick. By measuring the limiting area of spreading of a previously weighed drop of oil, Langmuir[3] calculated the number of molecules, N, per unit area of the film. Upon comparing the value of N for a number of oils belonging to a homologous organic series, such as the fatty acids, he found it to be the same for all members of the series. It did vary from series to series, however. Thus N for acetates is not the same as N for alcohols. With these data as a basis he showed conclusively that the oil films are but one molecule thick. Ordinarily the molecules of the film are closely grouped together in a single layer much like a layer of marbles grouped together on a table. Long molecules such as higher members of the fatty acid series have the active end, COOH, closest to the water, while the hydrocarbon chain projects approximately at right angles away from the water surface. Thus in the case of stearic acid,



the active group $-COOH$ dips into the water, while the hydrocarbon group of 17 carbon atoms projects away from it.

II. THE LANGMIUR MOVING-BARRIER APPARATUS

Langmuir devised an apparatus by means of which the film was compressed at the boundaries by a measured force per unit length, F. A graph of F as a function of N, the number of molecules per unit area of film, showed one or more points of discontinuity in the slope. In Fig. 1 is shown the sort of curve obtained for myristic acid.

N. K. Adam and later E. Rideal and their collaborators[4a, b] elaborated Langmuir's methods and made extensive applications of the F–N curves obtained to the study of monomolecular films and to the analysis of numerous organic structures. The latter application is possible because as N is increased the graph of F against N may exhibit changes of slope caused by rearrangements in orientation of the often complex-shaped molecules in order to be in a state of minimum energy.

[1] H. Devaux, J. de Physique **2**, 273 (1931).
[2] A. Pockels, Ann. d. Physik und Chemie **67**, 668 (1899).
[3] I. Langmuir, J. Am. Chem. Soc. **39**, 1848 (1917).
[4a] N. K. Adam and collaborators, Proc. Roy. Soc. A, 1921 to date.
[4b] E. Rideal and collaborators, Proc. Roy. Soc. A, 1925 to date.

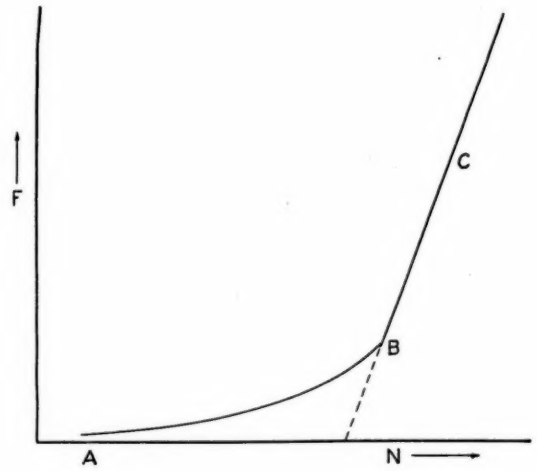


FIG. 1. Force-area curve for myristic acid at 5C.

III. THE ELECTRICAL PROPERTIES OF MONOMOLECULAR FILMS

The oils forming monomolecular films appear always to be characterized by the presence in the individual molecule of groups of atoms such as $-OH$, or $C=O$, or $C\equiv N$, known to possess electrostatic moments. Because of the parallel orientation of the molecules in the film we may find it possible to measure the electrical moments of individual molecules by studying the electrical field about the film.

If the component of the electrical moment of the molecule perpendicular to the surface of the water is u, and if dV is the change in potential in passing through the film, a well-known theorem of potential theory states that $dV=4\pi uN$.

In order to measure dV, M. J. Guyot[5] developed a method due to Righi[6] which had previously been used to measure the Volta potential difference between two metals. The two metal electrodes separated by an air gap are in series with a sensitive electrometer and a potentiometer. The air space between is radiated with alpha-particles from some radioactive substance. The alpha-particles ionize the gas, and because of the electrical field between the electrodes set up by the Volta electricity the ions migrate to the electrodes causing an electrometer deflection. By adjusting the potential until no electrometer deflection occurs, one measures the Volta potential difference. Guyot first measured the potential difference between water and a metal electrode held in the air just above the surface of the water. He next measured the potential difference when the water was covered by an oil film. The difference between the two measurements was regarded as the potential jump in passing through the oil film.

Schulman and Rideal[7] and later Adam and Harding[8] measured dV with an apparatus similar to that of Guyot. They found the graphs of dV against N to be of great value in the study of monomolecular films. Hughes[9] found it an interesting tool for the study of proteins, and recently Fosbinder and Lessig[10, 11] applied this technique to the study of stearolactone and a number of proteins such as pepsin, casein. They have also indicated a possible application to the study of enzyme reactions.

As might have been expected, the moments u computed from $dV=4\pi uN$ are always less than those found by applying the Debye theory to the temperature variation of the dielectric constant of gases. The polar molecules of water nearest the oil film orient, too, causing the observed dV to be due to the combined effect of the oriented molecules of the film and the oriented water molecules. The water molecules orient with their electrical axes directed opposite to those of the oil molecules. Hence the observed dV is smaller than that caused by the oil film alone, and consequently the computed polar moments are too small. Although as yet it has not been possible from the measurement of dV to obtain true moments, it has been found that substances of large moments have large values of dV. Also, as N is increased by increasing F with the Langmuir apparatus, we can study the effect of closer packing of the molecules on the measured dV, and thus can arrive at interesting conclusions concerning the presence and relative positions of the polar groups within the molecules.

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[5] H. Guyot, Ann. de Physique **10**, 508 (1924).
[6] Righi, J. de Physique 2, **7**, 153 (1888).

[7] Schulman and Rideal, Proc. Roy. Soc. **A130**, 259, 431 (1931).
[8] Adam and Harding, Proc. Roy. Soc. **A138**, 411 (1932).
[9] A. Hughes, Trans. Far. Soc. **29**, 211 (1933).
[10] Fosbinder and Lessig, J. Frank. Inst. **215**, 425 (1933).
[11] Fosbinder and Lessig, J. Frank. Inst. **215**, 572 (1933).

The method of Guyot suffers from several faults, the most serious of which are the bother of dealing with radioactive substances and sensitive electrometer and the difficulty of obtaining adequate electrical insulation for use with a sensitive electrometer when maintained near a water bath.

IV. The Experimental Apparatus

The method to be described is essentially that previously developed by one of us[12] and later used by us[13] to study the Volta potential difference between a gold electrode and a cleaved single crystal of zinc.

The electrical arrangement employed is shown in Fig. 2. The two metals A and B whose Volta

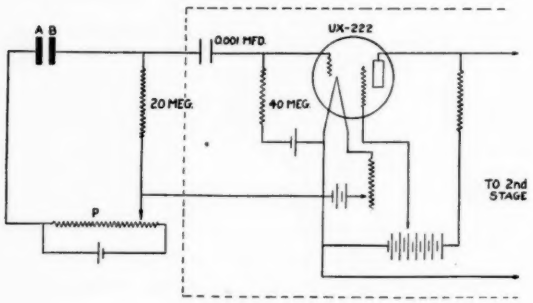

Fig. 2. Electrical circuit diagram.

potential difference is desired are arranged to form a parallel-plate condenser, the capacity of which is changed periodically by varying the separation of the plates. As the potential difference V is independent of the distance between the plates, and the capacity C is a periodic function of the time, and as the charge q on either plate is $q=CV$, there is an alternating current between A and B. This current is detected by connecting in the circuit an audiofrequency amplifier to the output of which a telephone is connected. By adjusting the potential difference applied to A and B by means of the potentiometer until no signal is heard one readily measures the Volta e.m.f., since it is then equal in magnitude and opposite in polarity to the potentiometer reading.

[12] W. A. Zisman, Rev. Sci. Inst. **3**, 367 (1932).
[13] W. A. Zisman and H. G. Yamins, Physics **4**, 7 (1933).

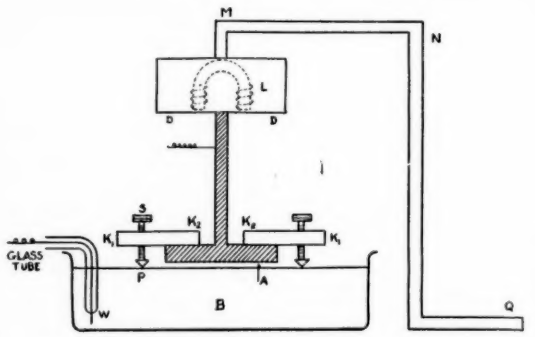

Fig. 3. Vibrating condenser for studying Volta effect in liquids.

The experimental arrangement employed to measure dV by this method is shown simply in Fig. 3. A flat gold electrode A is adjusted with its plane parallel to the water surface B. The water, even when prepared in a tin-lined still, is a sufficiently good conductor as compared with the 20-megohm resistance (see Fig. 2) so that a platinum wire, W, dipping into it suffices to make the electrical circuit complete. Of course, it is not a reversible electrode, but that is not needed for the purpose for which this apparatus is designed, since the only requirement this electrode must fulfill is that the potential difference between it and water remain constant for the few minutes needed to make measurements of the potential difference between A and B without and then with the oil film. Electrode A is vibrated to and away from the water surface by attaching it to an insulated rod which is fastened to the center of the flexible diaphragm, DD, of a loudspeaker vibrator, L, such as is used in radio sets. The vibrator was driven by current from a vacuum-tube oscillator at 250–500 cycles per second. It is necessary for high sensitivity to place A as close to the water surface as possible without causing contact. This adjustment is less critical the better the amplifier used. There is no doubt that a much greater gain in amplification can be obtained than that given by our apparatus. We obtained a sensitivity of 0.001 volt in the measurements of dV to be described. With the amplifiers and vacuum tubes now available a much greater sensitivity probably is obtainable.

Several details of technique may prove of interest. The water was contained in a Pyrex tray

about 5 inches in diameter placed upon a miniature three-legged table, one leg of which was capable of a fine screw adjustment so as to vary its height. After the potential difference between the free water surface and gold had been measured, the water surface was removed to a greater distance from the gold by adjustment of the height of the third leg. This permitted addition of the oil film by touching the water surface with a glass rod previously dipped in the oil. Such a procedure prevents chance water ripples from touching the gold electrode. After the addition of the oil film, the table leg was raised in order to make possible the measurement of the potential difference between the oil film and the gold. Three rubber hemispheres were cemented to the upper surface of the table to furnish a stable support for the Pyrex tray.

The adjustment of parallelism between A and B was accomplished by suspending the loudspeaker unit L from a frame MNQ which rested upon three feet Q_1, Q_2, Q_3 of which two, Q_1 and Q_3 were adjustable screws. The Pyrex tray upon Table T was placed as shown in Fig. 4. The plane

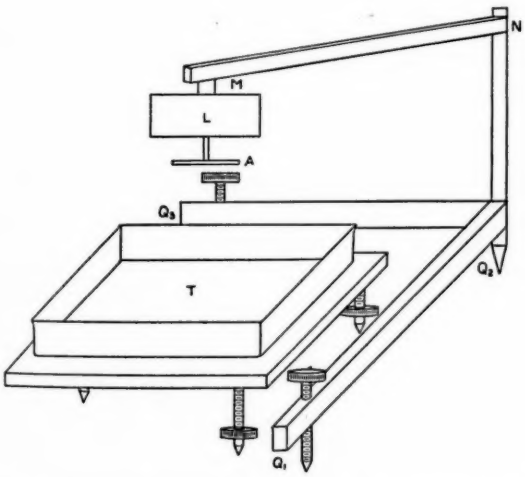

FIG. 4. General arrangement of vibrating condenser and tray.

of A could be easily and finely adjusted by rotation of screws Q_1 and Q_3. It was also found advantageous to have a means of coarse adjustment of the separation and tilt of A and B. We employed a ball and socket joint at the end M of bar MN and made it so that the length from L to M could be quickly varied about one inch by the sliding of a metal rod in a hole drilled through the ball.

The presence of a convex meniscus at the boundary of contact between water and glass tray makes it impossible to look through the glass side of the tray along the surface of the water and so watch the illuminated slit formed by throwing a beam of light through the air space between the gold electrode and the water. This prevents accurate adjustment of parallelism between A and B when they are quite close. The following was found to be an excellent substitute. Upon the upper surface of the gold electrode are cemented three thin slips of Bakelite KK (see Fig. 3) so that they form three spokes 120 degrees apart. Near the end of each is a fine screw SP, the polished point of which is in the same plane as the under surface of the gold electrode. By tilting the frame MNQ and adjusting the height of the third table leg until each screw point seems about to touch its image reflected in the water, a fine adjustment for parallelism is readily obtained.

The careful electrical shielding of this apparatus is essential. The metal case of the amplifier, the metal housing about the vibrator, L, and the frame MNQ should all be earthed. The wire connecting the electrode B to the grid of the first vacuum tube (see Fig. 2) should be enclosed in a grounded metal cable.

The uniform cleanliness of the gold electrode is important. If the electrode is not clean, the zero intensity of sound is not obtainable, and consequently the ease of measurement is considerably decreased. The electrode was therefore washed occasionally with ether and allowed to dry thoroughly before being used. If the surface of the oil film is not uniform, it is immediately indicated by the poor minimum of intensity of sound at balance. This is a new and valuable feature not possessed by Guyot's apparatus.

The Pyrex tray and platinum wire electrodes were cleaned before each new determination of dV by washing with a strong alkaline solution followed by a solution of potassium dichromate in concentrated sulphuric acid and several final rinsings with grease-free distilled water.

V. Results

(A) Time changes in measurements

The potential difference between gold and water covered with a monomolecular film of oil was found to be independent of the time for intervals ranging up to sixty minutes after formation of the film.

There is a small change with time in the potential difference between the gold and distilled water. It occurs in the first several minutes and amounts to a rise in that time of about 0.005 volt. After that the measurements are constant for twenty or more minutes. With the steady-state value, this potential difference was found to be repeatable to within 0.003 volt usually, provided the water was always obtained from the same still,

If the gold was removed from proximity to the water surface and a few minutes afterwards was brought close again in order to make new measurements, the same sort of rise with time of 0.005 volt occurred. Evidently, this effect must be caused by a slight shift in the potential of the gold due to a condensation of water upon it. Effects of the same order of magnitude were demonstrated to exist in our previous work on the Volta effect in zinc crystals.[13] Blowing water vapor at the newly cleaved crystal caused a rapid shift in the Volta potential difference of about 0.005 volt, but this effect disappeared completely in a few minutes if the condensed water was allowed to evaporate. This effect can be diminished by using greater amplification so as to enable good measurements to be taken with the electrode adjusted further away from the water surface. However, the error in the value of dV is less than 0.005 volt, since the closeness of gold electrode and oil-covered surface prevents evaporation of all the condensed water from the gold.

The values of dV used here were found by employing the steady-state values of the potential differences.

(B) Reproducibility

The values of dV obtained by us were found to be reproducible in a highly satisfactory manner as the following data show. The distilled water was always freshly prepared in a new tin-lined still. The measurements were all made at 22°C.

Three independent runs were made with oleic acid on distilled water. The results were:

Run	1	2	3
dV (volts)	0.163	0.162	0.165

Pure benzene was prepared by triply distilling Kahlbaum's "molecular weight" benzene. Two trial measurements of the potential difference due to dropping this benzene upon water were made. No effect was observed, i.e., $dV=0$, even when the measurements were made as early as 2 minutes after adding the benzene. This proves either that the benzene evaporates without leaving a residue or else that it leaves a residue having no effect on the potential difference between gold and water.

As a further proof that monomolecular films on water may be safely formed by dissolving in benzene the substance to be studied and then placing the solution on the water, the following experiment is cited. Oleic acid was dissolved in benezene and several drops of the resulting solution were placed on distilled water. The resulting dV was 0.164 volt, in excellent agreement with the results given above which were obtained without the use of benzene.

A solution of Eastman palmitic acid in benzene when placed on water gave the following results:

Run	1	2
dV (volts)	0.291	0.298

Using 1/100 normal sulphuric acid instead of the water we obtained:

Run	1	2	3	4	5
dV (volts)	0.380	0.394	0.380	0.383	0.379

Tricaprylin prepared by Eastman was tried on distilled water. The results were:

Run	1	2
dV (volts)	0.407	0.408

It was then studied by using 1/100 normal sulphuric acid in place of the water.

Run	1
dV (volts)	0.426

Trimyristin prepared by Eastman and dissolved in benzene was placed on distilled water. We found $dV=0.612$ volt. With 1/100 normal sulphuric acid in place of the water dV was 0.621 volt.

(C) Comparison with the results of Guyot

In Table I are presented the results of Guyot and ours for the purpose of comparison. His measurements were made at 18°C while ours were at 22°C.

TABLE I.

Substance	dV (Guyot) (volts)	dV (ours) (volts)
Oleic acid on distilled water	0.157	0.163
Palmitic acid on distilled water	0.290	0.295
Palmitic acid on dil. H_2SO_4	0.396	0.383
Tricaprylin on distilled water	0.412	0.408
Tricaprylin on dil. H_2SO_4	0.418	0.426
Trimyristin on distilled water	0.620	0.612
Trimyristin on dil. H_2SO_4	0.618	0.621

Our results are in very good agreement with Guyot's. We also have verified his conclusion that whereas dV for fatty acids is greatly affected by the presence of sulphuric acid, it is but slightly affected for substances like tricaprylin, trimyristin, and trilaurin.

ACKNOWLEDGMENTS

We wish to express to the Department of Physics of Harvard University our appreciation for their courtesy in permitting us to carry out these experiments in their laboratories. It is a pleasure to thank Professor J. B. Conant of the Department of Chemistry for his interest and for so generously placing at our disposal his supply of members of the series of fatty acids.

Analysis of Rotatory Dispersion Curves of Configurationally Related Fatty Acids[1]

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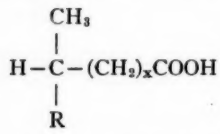
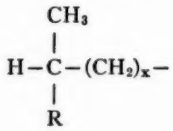
(THE CONTRIBUTION OF MR. MARKER WAS LIMITED TO THE PREPARATION OF SUBSTANCES)

(Received June 12, 1933)

The dispersion curves of fatty acids of the type



have been measured in the visible and in the ultraviolet regions with a view to establishing the sign and the magnitude of the contribution of the radicals



and $-COOH$ to the total rotation. The variables were R and x, the latter varying from 0 to 2. It was found that the increase of the chain of R had no effect on the sign of the contributions. The change of x from 0 to 1 or 2 resulted in a change of sign of the contribution of $-COOH$, leaving the sign of the other contribution unchanged. For 4 of the compounds it was possible to determine with precision the values of each of the two contributions.

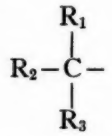
THERE is comparatively little experimental material on rotatory dispersion extending far into the ultraviolet region of organic compounds and therefore no general rules correlating chemical structure with optical activity could be established to this date. Recently, Werner Kuhn[2] suggested a simple model on which the newer theories of rotatory dispersion were developed in a comparatively simple manner and he, in cooperation with Freudenberg, applied his theoretical conceptions in order to evaluate the contributions of the individual constituents of the molecule to the total rotation.[3] The number of substances thus far analyzed in this manner is as yet small and the conclusions reached by Kuhn and Freudenberg in the case of isolated substances cannot as yet be generalized.

Kuhn has presented his theory in a number of publications and hence it need not be given here. For convenience of discussion, however, his terminology and his principal conclusions are recapitulated.

Given a simple molecule of the type

I.

(where X is a group or an element with an absorption band in the visible or in the near ultraviolet and R_1, R_2 and R_3 are simple alkyl groups with absorption bands in the Schumann region) and discussing the rotatory contribution of X, Kuhn in his terminology refers to its anisotropy as *induced* anisotropy, whereas the function of the radical



which induces the anisotropy is referred to as the *vicinal* function.

[1] For preliminary publication, see P. A. Levene and Alexandre Rothen, J. Am. Chem. Soc. **55**, 429 (1933).

[2] W. Kuhn and K. Freudenberg, *Hand und Jahrbuch der chemischen Physik.* "Drehung der Polarisationsebene des Lichtes." Leipzig (1932).

[3] W. Kuhn and K. Freudenberg, Ref. 2, §26, p. 81.

Kuhn stresses the point that the rotatory power of a given molecule is the sum of at least two terms. His original dispersion formulae for each term were similar to the general Drude formulae. More recently Kuhn has proposed a new dispersion formula by using an exponential expression for the absorption curve which is in better agreement with experimental data than the classical "damping" formula. In the simplest case, therefore, the rotation of each molecule may be regarded as the algebraic sum of two contributions, that of the group with the absorption band nearest to the visible and that of the sum of the remaining groups.

Kuhn arrives at the following conclusions in regard to each of the two contributions:

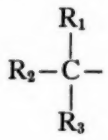
(1) The band in the visible or in the ultraviolet nearest to the visible (weak band) furnishes the major contribution to the rotation in the visible. (However, he reports individual cases in which this is not so.)

(2) The vicinal action of a group, in regard to the rotation in the visible, is due mainly to its strong Schumann bands.

(3) Small changes in the groups with the absorption bands in the more distant ultraviolet region do not alter the sign of the induced anisotropy of the nearest band.

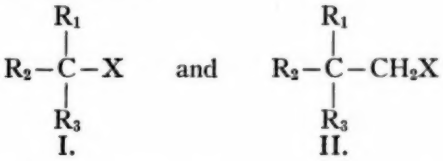
(4) The value of the contribution of a group located at a certain distance from the asymmetric center and possessing an absorption band in the near ultraviolet is not greater than that of a simple alkyl group.

Kuhn himself was cognizant of the lack of precision in the majority of his conclusions. Thus, he emphasizes the difficulty of defining the type of change which is to be classified under the term "small change" and therefore the difficulty of predicting the sign of the induced anisotropy from the structure of the inducing groups. Likewise, the theory does not furnish information as to whether the identical radical



induces anisotropy-factors of the same sign regardless of the character of the group or the atom with the weak absorption band. Furthermore, the rule of distance is expressed in very indefinite terms and states nothing of the possible changes with distance of the sign of anisotropy or of the possible alternation in the value of the anisotropy-factor of the group.

A more exact knowledge of the effect of the distance from the asymmetric carbon on the character of the induced anisotropy of a group would be of great assistance for the purpose of establishing the sign of the anisotropy-factor induced in different groups or elements by an identical radical. The reason is evident. Given the two substances

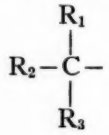


I. and II.

the first, on substitution of X by Y, may or may not preserve its original configuration, whereas the second one definitely does. Hence, a difference in the sign of the anisotropy of X and Y, if such should occur on substitution of X by Y in substance I, could be attributed to two alternative causes, either to differences in the absorption bands in X and Y or to a Walden inversion having taken place in the course of the reaction of substitution; in substance II, the change could be attributed only to the first-mentioned cause. If a precise knowledge of the effect of distance on the anisotropy of a group could be established, then from the effect of substitution in substances of type II, information could be obtained as to the effect of the identical substitution in substances of type I.

Fortunately, in certain substances of the general formulae I and II, it is possible to correlate their configurations by direct chemical methods without involving a reaction of substitution. In substances of this type it is possible to detect the existence or non-existence of change in sign of the factor of anisotropy of a given group when it is removed from the center of asymmetry by one or more carbon atoms. Should definite rules in this respect be discovered, it would be possible to correlate the configurations of substances of types I and II in cases where direct chemical methods are not available.

Such information would then be the basis on which the vicinal effects of one radical



on different groups or elements could be established.

These considerations led us to undertake a systematic study of the induced anisotropy in a given group as a function of its distance from the asymmetric center.

Methods of Analysis

The direct method of evaluation of the rotatory contribution of a given band of a given molecule consists in measuring its circular dichroism. This method is available when the band is situated in the visible or in the near ultraviolet region of the spectrum and when the ratio $(\epsilon_l-\epsilon_r)/\epsilon$ is sufficiently large to permit measurements of circular dichroism. (ϵ_l and ϵ_r are the extinction coefficients for left and right circular polarized light, respectively, $\epsilon_l-\epsilon_r$=circular dichroism and ϵ=extinction coefficient of the band.)

When this method is not available, an estimation of the direction and in some instances of the numerical values of each rotatory contribution can be obtained from the dispersion curve of the given substance. For this analysis the assumption is made that, as a first approximation, the dispersion curve at some distance from an absorption band can be expressed by two simple Drude terms. Under the dispersion curve in this instance is understood the graph of the function $((1/\alpha), \lambda^2)$.

The curvature of this graph varies in a definite manner depending upon the relationship of the term $A_1/(\lambda^2-\lambda_1^2)$ to $A_2/(\lambda^2-\lambda_2^2)$ (members of the two Drude term equation) as was definitely shown by Hunter.[4] It is evident that for very small intervals of the dispersion curve it is possible to find an expression $A_0/(\lambda^2-\lambda_0^2)$ which can very nearly satisfy the right-hand term of the expression

$$[M]=A_1/(\lambda^2-\lambda_1^2)\pm A_2/(\lambda^2-\lambda_2^2).$$

[4] H. Hunter, J. Chem. Soc. **125**, 1198 (1924).

The value of λ_0 and its variation with successive small wave-length intervals will provide the required information on the relative values of the four constants of the two Drude term formula.

Four combinations have to be considered in the discussion of the relationship of the dispersion curves to the relative values of the two terms. They are as follows:

Two terms of same sign (for long wave-lengths).

(1) $\lambda_1>\lambda_2[A_1/(\lambda^2-\lambda_1^2)]>A_2/(\lambda^2-\lambda_2^2)$

(2) $\lambda_1>\lambda_2[A_1/(\lambda^2-\lambda_1^2)]<A_2/(\lambda^2-\lambda_2^2)$.

Two terms of opposite sign (for long wave-lengths).

(3) $\lambda_1>\lambda_2[A_1/(\lambda^2-\lambda_1^2)]>A_2/(\lambda^2-\lambda_2^2)$

(4) $\lambda_1>\lambda_2[A_1/(\lambda^2-\lambda_1^2)]<A_2/(\lambda^2-\lambda_2^2)$.

Case 1

The resulting curve is practically a straight line for the long wave-lengths, the curvature becoming more pronounced for λ approaching λ_1. The values of λ_0 lie in between λ_1 and $\lambda_2(\lambda_2<\lambda_0<\lambda_1)$ and are progressively shifted towards λ_1 for smaller wave-lengths.

Case 2

This is similar to 1 but the curvature is accentuated. The displacements of λ_0 are greater but we still have the condition $\lambda_2<\lambda_0<\lambda_1$.

Case 3

We have here the condition $\lambda_2<\lambda_1<\lambda_0$. On the small wave-lengths side we observe a displacement of λ_0 towards λ_1. The curve in general will deviate from a straight line more than in cases 1 and 2. The apparent shift of λ_0 may be considerable when the whole spectrum is considered. Rotations in the visible region may lead to λ_0 values 1500A higher than that obtained from rotation in the ultraviolet. (The more so, the more nearly A_1 and A_2 approach the same magnitude.) (See Table XI.)

Case 4

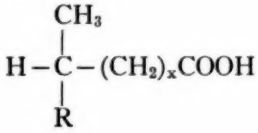
With decreasing wave-lengths, the curve shows first a minimum at $\lambda_m(\lambda_2<\lambda_1<\lambda_m)$, then increases to $+\infty$, reappears at $-\infty$ and ap-

proaches zero for the smaller wave-lengths. (The rotation goes through a maximum, decreases, reaches a zero value and increases in the opposite direction.) The λ_0 values calculated from measurements in the long wave-lengths region are smaller than $\lambda_2(\lambda_0<\lambda_2<\lambda_1)$ and become negative for λ values approaching λ_m.

From this analysis it follows that the graph $((1/\alpha), \lambda^2)$ leads to information as to the direction of rotation of each of the two contributions and of their relative values.

Statement of the Specific Problem

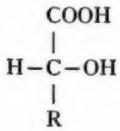
The present paper is concerned with the analysis of the series of disubstituted carboxylic acids of the general type



(x varied from 0 to 2 and R varied from C_2H_5 to $C_{10}H_{21}$). In Table I are given the maximum rotations of the members of several homologous series of configurationally related disubstituted carboxylic acids. The correlation was established by direct chemical methods.[5, 6] In the series of acids given in Table I some are dextrorotatory and others are levorotatory. In those that have been studied, the carboxyl group was found to be anisotropic inasmuch as the rotatory dispersion curves of these substances were distinctly different from those of the optically active trisubstituted methanes. It is therefore warranted to regard the carboxyl group as furnishing one contribution to the rotation in the visible by the anisotropy of its absorption band or bands whereas the rest of the molecule furnishes the sum of the other contributions. A new group of bands characteristic for COOH has recently been located at 1750A, in addition to the formerly known band at $\lambda = 2000$–2100A.[7] This fact is important to bear in mind in order to explain the direction of the rotatory contribution of the carboxyl group in the series of acids given in Table I.

[5] P. A. Levene and R. E. Marker, J. Biol. Chem. **91**, 77 (1931); **25**, 153 (1932); **98**, 1 (1932).

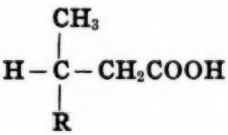
[6] The configurations are related among themselves and have no bearing on the configuration of acids of the type



Results of the Analysis of the Rotatory Dispersion Curves

I. Disubstituted acetic acids and their corresponding ethyl esters

In the case of the members of this homologous series, the dispersion curves may be expressed from the visible far into the ultraviolet region by a single Drude term, the λ_0 value being the same for all members and equal to 1850A. In the case of the propionic acid series, the λ_0 of the first member of the two term expression was found to be $\backsimeq$2000A, which corresponds to the position of the first absorption band of the carboxyl group. The λ_0 corresponding to the esters of the acetic acid series derivatives are even lower (1550 and 1480A for the ethyl esters of α-methylbutyric and α-methylvaleric acids, respectively). The only conclusion to be drawn is that their curves belong to the type described above under (1) or (2), i.e., two Drude terms of the same sign. The apparent validity of one Drude term to express the dispersion with a fair degree of accuracy over a considerable region of the spectrum (from 6000 to 2400A) is explainable on two alternate assumptions: first, that the contribution of the first band of the COOH or $COOC_2H_5$ ($\lambda \backsimeq 2000$A) is very small in comparison with the contribution of the rest of the molecule; second, that not this band but the second band of the COOH group ($\lambda \backsimeq 1750$A) furnishes the first contribution. This question could be solved by a study of the dichroism in the region of 2000A.

II. Homologous series 

As compared with the series of disubstituted acetic acids, this series is more complex and more instructive. From Table I it will be seen

[7] G. Scheibe, F. Povenz, and G. F. Lindstrom, Zeits. f. physik. Chemie **B20**, 283 (1933).

that in the visible region the rotations of the members of this series differ from those of the previous one in two respects: first, not all members of this series rotate in the same direction as is the case in the acetic acid series; second, the values of the rotations of the individual members of this series are lower than those of the corresponding members of the previous series. The analysis of the dispersion curve gives a ready explanation of both peculiarities.

(a) *The case of the first member.* The curves expressing the dispersion of the acid and of its ester represent a typical example of case 4, above. The experimental values agree well with those calculated by a formula of this type (see Fig. 1, curves 1 and 2, Fig. 2, Table VII and Table VIII). The position of λ_1(2050A) corresponds to the known first absorption band of the COOH group. For λ_{5893}, for instance, the first contribution (COOH) in the case of β-methylvaleric acid is 70 percent of the sum of the other contributions. The dispersion curve shows a typical abnormal course reaching a minimum ($\lambda_m = 2860$A) which is followed for smaller wave-lengths by a sharp rise in the $1/[M]$ values.

The value ($\lambda_m = 2860$A) calculated for the position of the minimum of the dispersion curve is easily obtained by equating the first derivative of the dispersion equation to zero.

$$\frac{11.68}{(\lambda_m^2 - 0.034)^2} - \frac{8.088}{(\lambda_m^2 - 0.042)^2} = 0.$$

This is a good example to demonstrate that, although the dispersion in the visible region can be accurately expressed by one Drude term, the λ_0 value found (1120A) has no significance since the dispersion in the ultraviolet definitely proves the presence of two terms of opposite sign, the value of the second term for the visible region being greater than that of the first.

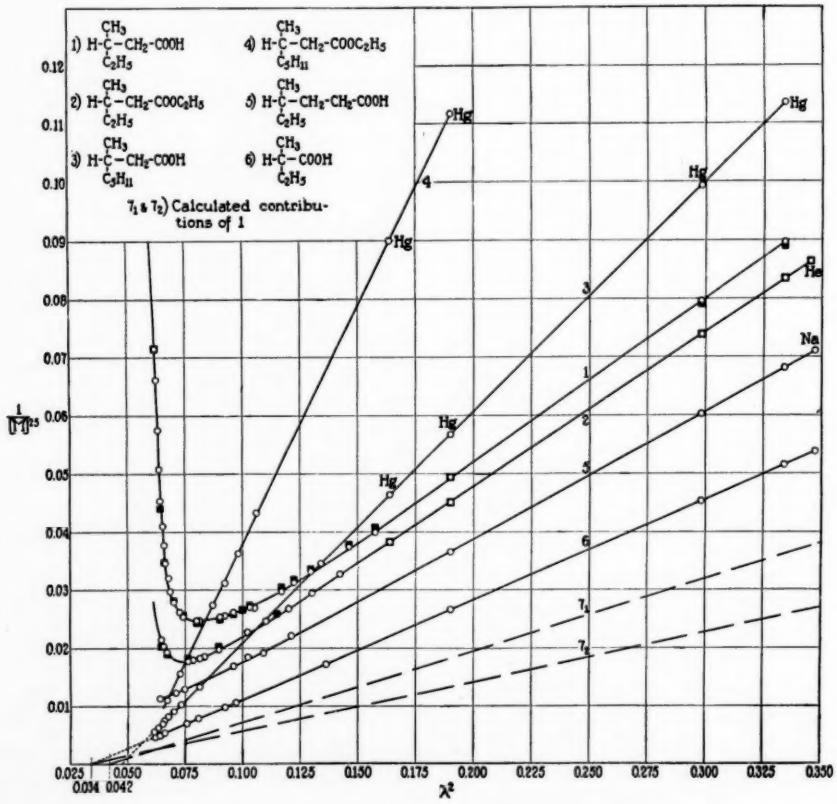


FIG. 1. Examples of the most characteristic dispersion curves. Circles represent experimental values, solid squares, calculated.

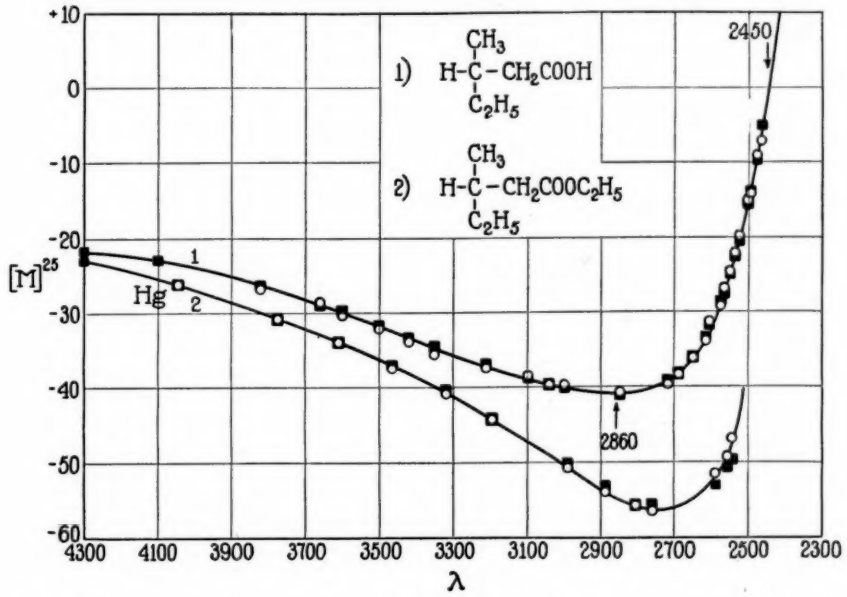


FIG. 2. Dispersions of two compounds exhibiting typical abnormality. Circles represent experimental values, solid squares, values calculated from a two Drude term formula (Tables VII and VIII).

The values calculated from a two Drude term formula valid for the ultraviolet region are about 0.5 percent higher than the experimental figures for $\lambda > 4500$A.

It will be seen from the comparison of the figures in the third and fourth columns of Table VIII that the rotations of the ester in the visible region, like those of the corresponding acid, can be represented within 0.1 percent by *one* Drude term. The λ_0 value has, of course, no physical significance. The values calculated from a two Drude term formula, valid for the ultraviolet region, may be seen in the fifth column. The magnitude of both terms has been indicated for the visible region to show how the observed rotation is but a small fraction of the rotation of each term.

The agreement between calculated and observed rotations is very good if we consider that for the small wave-lengths, the observed rotation is only one-tenth of the value of each Drude term.

(b) *The case of the higher members.* The character of the dispersion curves of these members is more pronounced in their esters. The curves belong to type 3. The ethyl ester of β-methylcaproic acid is a very good example of the limiting case in which the value of A_1 approaches that of A_2. For this substance, even in the visible region, the dispersion cannot be expressed by the one Drude term formula. The apparent λ_0 for the one Drude term formula is 3630A, calculated from the values $[M]^{25}_{5780}$ and $[M]^{25}_{4358}$, thus showing a striking shift from the position of the first absorption band. As expected, the rotatory dispersion curves present a strong convex curvature. Even in the visible, discrepancies as high as 20 percent are obtained between rotations calculated from a one Drude term formula and the observed value. (See Table XI.)

The low rotatory values observed in the visible region for this substance are due not to the low anisotropy factors of the absorption bands but to the fact that the two contributions are of opposite sign, the two constants A_1 and A_2 being nearly equal.

For values of λ approaching λ_1, the first term, $A_1/(\lambda^2-\lambda_1^2)$, becomes predominant and the observed rotation practically represents the contribution of the first term. This is well demonstrated by a comparison of the dispersion of the ethyl ester of β-methylcaproic acid with that of the ethyl ester of β-methylcaprylic acid. (See Tables XI and XIV.)

$$\frac{[M]^{25}_{5780}\ \beta\text{-methylcaproic ethyl ester}}{[M]^{25}_{5780}\ \beta\text{-methylcaprylic ethyl ester}} = 0.173$$

and

$$\frac{[M]^{25}_{2600}\ \beta\text{-methylcaproic ethyl ester}}{[M]^{25}_{2600}\ \beta\text{-methylcaprylic ethyl ester}} = 0.918.$$

In other words, the anisotropy-factor of the $COOC_2H_5$ group of those two compounds is of the same order of magnitude although the rotation observed in the visible region is four times greater for β-methylcaprylic ethyl ester than for β-methylcaproic ethyl ester.

It is noteworthy that the calculated λ_1^2 of the first term of the two Drude term formulae, expressing the experimental dispersion curves of the β-methylcaproic and β-methylcaprylic esters is higher than the λ_1^2 found for β-methylvaleric acid (0.052 compared to 0.042). It is realized that too great significance should not be attached to this difference since it is possible to obtain a fair agreement of the experimental data by changing correspondingly in each formula the λ_0 values of both terms. Nevertheless, this difference does seem to be real. It should be noted here that results recently published[8] show that a shift of the first band is observed (from about 2030A to about 2130A) when the absorption of acetic acid is compared with that of its ethyl ester.

As may be seen from Table XIII, the dispersion of β-methylcaprylic acid in the ultraviolet region may be well expressed by one Drude term with a λ_0^2 value (0.0484) noticeably higher than the λ_0^2(0.0455) obtained from measurements in the visible region. In other words, the dispersion curve is not a straight line over the entire spectrum and the curvature is concave instead of convex as would have been expected for two terms of opposite sign. However, on account of the high value obtained for λ_0^2 it would appear that the first two terms do not have the same sign. It is possible that the second term departs strongly from a linear relation but there is also the possibility that the dispersion due to a single band is greater than that required by a formula of the type $A/(\lambda^2-\lambda_0^2)$.[9] Nevertheless, the contribution of the first band undoubtedly has the sign of the observed rotation. This is the important fact which is revealed by our experiments.

(c) *Cause of the differences in rotation in the visible between the first and the higher members of this series.* From the foregoing considerations it is apparent that the differences in the direction of rotation in the visible between the first and the higher members is due not to the differences in the sign of the factors of anisotropy of the COOH absorption band of the respective members of the homologous series, but to the fact that in the case of the first member, the second contribution predominates in the rotation in the visible region of the spectrum whereas in the higher members the first contribution (the carboxyl) predominates.

III. Series $H-\overset{\overset{CH_3}{|}}{\underset{\underset{R}{|}}{C}}-CH_2CH_2COOH$

All members of this series rotate in the visible part of the spectrum in the same direction. Rotatory dispersion measurements were made on one member only (see Table XV and Fig. 2, curve 5). The dispersion curve belongs to the same type as the first member of the preceding series. There is no doubt that a minimum could be detected if the curve could be extended sufficiently far into the ultraviolet.

From the values in the last three rows of Table XV it may be seen that this minimum must be very near 2530A. (The value calculated from the equation in column 5 is 2500A.) The absorption in this region, however, was too great to permit measurement of the rotation. As regards measurements in the visible region, the low value found for λ_0^2(0.021) is the only indication that the dispersion is truly expressed by two terms of Drude of opposite sign, the one with the greater wave-length being smaller than the other (case 4).

Although there are two carbon atoms between

[8] H. Ley and G. Arends, Zeits. f. physik. Chemie **B17**, 177 (1932).

[9] W. Kuhn and K. Freudenberg, Ref. 2, pp. 76–79.

the asymmetric carbon atom and the carboxyl group, the anisotropy of the latter is still very important, its contribution being roughly 50 percent of that of the rest of the molecule.

In view of the fact that the direction of rotation is identical for all members of this homologous series, it is admissible to conclude that in all of them the two contributions are of opposite sign, the second contribution having the greater value for the visible and for the near ultraviolet regions.

General Conclusions

(1) In each of the three homologous series, acetic, propionic and butyric, the direction of rotation of each contribution remains constant in the entire series as long as R_1 is smaller than R_2 or *vice versa*, even in the case when the directions of rotation of individual members in the visible region of the spectrum are of opposite sign.

(2) The change of the distance of the groups COOH or $COOC_2H_5$ from the asymmetric center (by the introduction of CH_2 groups between the asymmetric carbon atom and the carboxyl group) has no effect on the direction of the second contribution which is furnished by the anisotropies of the bands located in the Schumann region. Kuhn has postulated that these groups contribute to the rotation in the visible principally by their vicinal effect and that this effect is not altered by small changes in their character. The direction of their own contribution, however, may change under these conditions. In the case of the substances here discussed, the direction of their contribution was not altered by the change of the distance of the anisotropic groups COOH or $COOC_2H_5$. Whether this is a general rule or applies only to the present series of substances, remains to be established.

(3) The change of the distance of the COOH or $COOC_2H_5$ groups from the asymmetric center brings about a change in the direction of the first contribution (carboxyl group) so that in the substituted acetic acids, the two contributions are of the same sign, whereas in the disubstituted propionic they are of opposite sign. Further increase in the distance of the COOH or $COOC_2H_5$ from the asymmetric carbon atom by CH_2 does not alter the signs of either one of the two contributions characteristic of the disubstituted propionic acids.

(4) The change of sign of the first contribution (carboxyl group) on passing from the acetic to the propionic acid series may be due to one of two causes: either to change of sign of the anisotropy-factor of the identical absorption band or to the circumstance that in each series a different band of the COOH group is rendered anisotropic. As yet no decision can be made between the two possibilities.

(5) More precision will have to be introduced in the formulation of the distance rule of Tschugaeff and Kuhn[10] inasmuch as the carboxyl group at considerable distance from the asymmetric carbon atom retains considerable anisotropy. It will be shown in a later publication that the same phenomenon holds for halides and for other groups or atoms with absorption bands in the near ultraviolet.

Experimental

Compounds

All the compounds were prepared as previously described.[5] It was necessary, of course, to obtain them in the highest possible state of purity. It may be mentioned that, in general, compounds directly resolved (e.g., the acids used here) are of a high degree of purity, as a result of the numerous recrystallizations required for the resolution. The acids were purified through their sodium salts. All the final distillations were made in all glass apparatus and the substances carefully fractionated. At least two fractions were made in the last distillation and the product was used only if the indices of refraction were the same for both fractions. All the *acids* were titrated. Analyses for C and H on each substance gave figures in agreement with the calculated values within the limits of experimental error (± 0.1 percent).

The preparation of β-methylcaproic acid was duplicated. Both products had the same physical constants (n_D^{25} and δ_4^{25}) and exhibited the same dispersion. Titration was the most sensitive test, indicating that all our compounds, with the possible exception of α-methyldodecylic acid

[10] W. Kuhn and K. Freudenberg, Ref. 2, §35, p. 111.

(accurate titration difficult), had a purity of at least 99.5 percent.

Solvent

N-Heptane was chosen for solvent, since it is the only hydrocarbon transparent in the ultraviolet region which is obtainable in large amounts in a pure state. The hexane, hitherto employed almost exclusively, is an ill-defined mixture of hydrocarbons. Before use, the *N*-heptane (obtained from California pine trees) was purified according to Henri.[11] After purification it had the following physical constants.

n_D^{25} 1.3850 δ^{25} 0.67943 B.P. 98.4°.

General

All $[M]$ values (molecular rotations) indicated, correspond to substances completely resolved. The molecular rotations were calculated from the usual formula $[M]=10\alpha/lc$ where c = concentration in mol per liter and l = length of the tube in decimeters. When substances not resolved to the maximum were used, the proper coefficient was applied in calculating $[M]$ from the experimental α. Maximum values for $\lambda=5893$ have been published previously by Levene and Marker[5] for all the acids presented in this communication. The absolute magnitudes of $[M]$ are only accurate to within a few percent but, of course, the dispersion measurements are of a much higher degree of accuracy (in the visible region from 0.1 percent to 0.01 percent, according to the magnitude of α).

All the $[M]$ values of the acids determined in heptane are 1 to 3 percent higher than in the homogeneous state.

Densities are expressed in g/ml (specific gravity 25/4 in vacuo).

Indices of refraction were determined with an Abbe refractometer accurately checked and are correct to ± 0.0001. Wave-lengths are expressed in Angstrom units but to comply with the usual convention they are given in microns in the Drude equations and in Fig. 1.

Measurements in the visible region

Rotatory measurements in the visible region were made with a large Schmidt and Haensch polariscope (Lippich type) reading to one-thousandth of a degree. The instrument was mounted on an optical bench permitting the use of 1-meter tubes. The half shadow angle adopted for all measurements was 3°. The apparatus was provided with a monochromator and color filter to eliminate the diffused light. All the measurements were carried out with monochromatic lights only. The sources were the following:

Hg arc (quartz lamp 6 amp.). Lines: 5790.7, 5769.6, 5460.7, 4358.3 and 4046.6. (For large values of α only, measurements were carried out with the lines 5790.7 and 5769.6 separately, the optical mean 5780.1 being used for most of the measurements.)

He arc. A hot cathode lamp, previously described, was found very satisfactory.[12] Lines: 6678.1 and 5875.6.

Na arc. The recently developed Osram sodium arc lamp was used. The line 5892.6 is much less intense than the yellow line obtained in the above-mentioned lamp.

To insure their correct position and thus eliminate the possibility of a shift of the zero of the apparatus, all these lamps were mounted on an optical bench.

Each α value given in the tables (for the yellow and green part of the spectrum) is the arithmetical mean of at least 20 readings, 10 for the empty tube and 10 for the tube when filled. The mean values of duplicate series of 10 readings agreed within 0.001°. When the angle to determine was very small, the mean values of duplicate series could be obtained within 0.0005 by exercising extra care. The zero position was determined for each wave-length separately. The shift of the zero position with wave-length could not be determined once and for all as it depended on the condition of strain of the glass and plates of the tubes. The rotation for 6678.1, 4358.3, 4046.6, were all photographically determined. The camera used for these determinations (see Fig. 3) consisted simply of a plateholder (6×9 cm) capable of vertical motion, by means of a rack and pinion in front of the eyepiece. No extra lens was necessary. In order to reduce the time exposure it was arranged that the images obtained were small (0.1 cm diam.); with Eastman plates No. 40, the time of exposure

[11] A. Castille and V. Henri, Bull. Soc. Chem. Biol. **6**, 299 (1924).

[12] A. Rothen, Science **74**, 204 (1931).

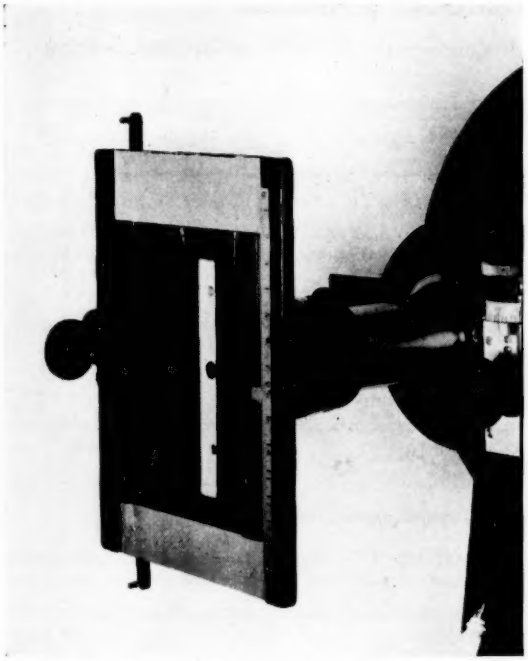


FIG. 3. Camera adjusted to the eyepiece of Schmidt and Haensch polariscope (Large Universal model)

corresponding to 4358.3 and 4046.6 was 10″ and 60″, respectively. For each determination a series of photographs was taken with settings of the analyzer 0.005° apart. The sensitivity obtained was 0.003° under the best conditions used. The photographs were examined with an ordinary binocular magnifying glass.

Temperature

All measurements were performed at 25°C. Water-jacketed tubes were used throughout. A thermostat (*ca.* 100 liters) in conjunction with a small pump ensured constant temperature of the polariscope tubes (25°C±0.02°). Variations greater than 0.02°C would have rendered useless all photographic measurements for heptane solutions in tubes 40 cm long, the variation in refraction thus produced being sufficient to outfocus the images on the photographic plate. The same temperature control was employed for measurements in the ultraviolet.

Measurements in the ultraviolet region

The apparatus used was of the type described by Kuhn.[13] The Rochon prisms (polarizer and analyzer) had the following dimensions, 1.5×1.5×3 cm. The angle between the direction of polarization of the two halves of the polarizer was 6°. The image of the surface of the polarizer was focussed on the slit of a medium size Hilger spectrograph No. E316 by means of a quartz-fluorspar lens having a focal length of 27 cm. The analyzer was mounted on a graduated circle reading to 0.01°. A condensed spark between two tungsten-steel electrodes was used as the source of light.

In estimating the error $\Delta\lambda$ made in the reading of λ for which the two half spectra have the same intensity on the photographic plate, the expression $1/(\Delta\lambda)=k\delta\alpha/(\delta\lambda)$ may be used as a first approximation. When both the rotation and the dispersion of the tested compound have large values, the coefficient $\delta\alpha/(\delta\lambda)$ is large and hence the error $\Delta\lambda$ is reduced.

The apparatus was checked with 2 quartz plates calibrated by the Bureau of Standards ($\alpha_{5461}{}^{20}=41.60°$ and $\alpha_{5461}{}^{20}=0.979$). The experimental values agreed well with the figures calculated from Lowry's equation.[14] The figures obtained for the plate $\alpha_{5461}{}^{20}=0.979$ (for which the readings were more difficult) were as follows:

α_{2320} = Found 7.30(calc. 7.28) α_{2685}
Found = 4.90(calc. 4.92).

α_{2940} = Found 3.90(calc. 3.93) α_{3330}
Found = 2.90(calc. 2.92).

As can be seen, the readings are correct to within a few hundredths of a degree.

TABLE I. *Maximum molecular rotations of configurationally related aliphatic acids without solvent*[15] $[M]^{25}_{5892.6}$.

α-Methylbutyric acid*	−18.0	γ-Methylcaproic acid*	−13.6
Ethyl ester*	−22.9		
α-Methylvaleric acid*	−21.4	γ-Methylheptylic acid	− 6.9
Ethyl ester*	−27.5		
α-Methylcaproic acid	−24.3	γ-Methylcaprylic acid	− 4.1
α-Methylnonylic acid	−27.3	γ-Methylnonylic acid	− 1.9
α-Methyldodecylic acid*	−27.5	δ-Methylheptylic acid	−11.1
β-Methylvaleric acid*	−10.4	δ-Methylcaprylic acid	− 3.7
Ethyl ester*	−11.5		
β-Methylcaproic acid*	+ 3.6	δ-Methylnonylic acid	− 1.7
Ethyl ester*	+ 0.69		
β-Methylheptylic acid*	+ 6.1	δ-Methyldecylic acid	− 0.6
β-Methylcaprylic acid*	+ 8.1	ε-Methylcaprylic acid	−12.2
Ethyl ester*	+ 4.1		

[13] W. Kuhn, Ber. chem. Ges. **62**, 1727 (1929).

[14] T. M. Lowry and W. R. C. Adams, Phil. Trans., Roy. Soc. **A226**, 391 (1927).

[15] Rotatory dispersion curves have been determined only for compounds marked with an asterisk.

TABLE II. *Rotatory dispersion of levo-α-methylbutyric acid in heptane.*

Constants of sample: $\delta_4^{25}=0.9340$, $n^{25}{}_D=1.4038$. Visible region:[16] Concentration 0.8543 M, $\delta_4^{25}=0.7030$, $l=40$ cm. U.V. region: Concentration 0.8563 M, $\delta_4^{25}=0.7030$, $l=10$ cm.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{5.8110}{\lambda^2-0.03526}$ [17]	λ	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{5.8110}{\lambda^2-0.03526}$
6678.1	− 3.98$_0$	−14.1$_5$	−14.1$_5$	3040	− 7.05	−100.0	−101.6
5892.6	− 3.237	−18.62$_1$	−18.62$_7$	2980	− 7.55	−107.1	−108.5
5780.1	− 5.469	−19.44$_6$	−19.44$_6$	2880	− 8.55	−121.3	−121.8
5460.7	− 6.217	−22.10$_4$	−22.10$_1$	2832	− 9.05	−128.4	−129.3
4358.3	−10.56$_5$	−37.56$_4$	−37.56$_4$	2745	−10.15	−144.0	−144.9
3690	− 4.05	−57.4	−57.6	2571	−13.05	−186.6	−188.4
3540	− 4.55	−64.6	−64.5	2529	−14.05	−200.8	−202.5
3410	− 5.05	−71.7	−71.7	2505	−14.55	−206.4	−209.5
3290	− 5.55	−78.8	−79.6	2490	−15.05	−215.0	−219.0
3115	− 6.55	−92.9	−94.1	2380	− 1.70 (1 cm)	−241	−272

TABLE III. *Rotatory dispersion of levo-ethyl ester of α-methylbutyric acid without solvent.*

Constants of sample: $\delta_4^{25}=0.8689$, $n^{25}{}_D=1.3973$. Visible region: $l=10$ cm. U.V. region: $l=5$ cm. Measurements on dextro form.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{7.2843}{\lambda^2-0.02923}$	λ	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{7.2843}{\lambda^2-0.02923}$
5780.1	−2.880	−23.89	−23.89	3275	−5.65	− 93.7	− 93.4
5460.7	−3.264	−27.08	−27.08	3175	−6.15	−102.$_0$	−101.$_8$
4358.3	−5.46$_3$	−45.3$_2$	−45.3$_2$	3090	−6.65	−110.$_3$	−110.$_6$
4046.6	−6.56$_0$	−54.2$_6$	−54.1$_5$	3010	−7.15	−118.$_6$	−118.$_7$
3590	−4.40	−73.0	−73.1	2910	−7.90	−131.$_1$	−131.$_4$
3380	−5.15	−85.5	−85.7	2883	−8.15	−135.$_2$	−135.$_2$
3330	−5.40	−89.6	−89.2	2585	−2.45 (1 cm)	−203	−194

TABLE IV. *Rotatory dispersion of levo-α-methylvaleric acid in heptane.*

Constant of sample: $n^{25}{}_D=1.4113$. Visible region: Concentration 0.7857$_7$ M, $\delta_4^{25}=0.7031$, $l=40$ cm. U.V. region: Concentration 0.8910$_3$ M, $\delta_4^{25}=0.7066$, $l=10$ cm.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{6.7499}{\lambda^2-0.03496}$	$[M]^{25}=-\frac{6.770}{\lambda^2-0.03458}$	λ	α^{25}	$[M^{25}]$	$[M]^{25}=-\frac{6.7499}{\lambda^2-0.03496}$	$[M]^{25}=-\frac{6.770}{\lambda^2-0.03458}$
6678.1	− 5.16	− 16.4$_1$	− 16.4$_2$	—	2835	−13.10	−147.0	−148.6	−147.8
5875.6	− 6.837	− 21.75$_0$	− 21.75$_5$	—	2727	−15.10	−169.4	−171.2	−170.1
5780.1	− 7.092	− 22.56$_1$	− 22.56$_4$	—	2644	−17.10	−191.9	−193.1	−191.5
5460.7	− 8.060$_5$	− 25.64$_2$	− 25.64$_2$	—	2605	−18.10	−203.1	−205.2	−203.3
4358.3	−13.69$_0$	− 43.55	− 43.55	—	2574	−19.10	−214.1	−215.7	−213.6
3910	− 5.10	− 57.2	− 57.2	− 57.2	2540	−20.10	−225.6	−228.4	−226.0
3774	− 5.60	− 62.8	− 62.8	− 62.7	2513	−21.10	−236.8	−239.4	−236.8
3173	− 9.10	−102.0	−102.7	−102.4	2488	−22.10	−248.0	−250.5	−247.7
2902	−12.10	−135.8	−137.0	−136.3	2420	− 2.60 (1 cm)	−280	−286	−282

[16] For all tables, under the term "visible region" we understand measurements made from 6678.1A. to 4046.6A., the rotations being observed with the large Schmidt and Haensch instrument. The term "U.V." comprises all measurements for $\lambda<4046.6$A.

[17] Lowry (Soc. **103**, 1074 (1914)) gives 0.0375 for λ_0^2 from measurements in homogeneous state in the visible region.

TABLE V. *Rotatory dispersion of levo-ethyl ester of α-methylvaleric acid without solvent.*

Constants of sample: $\delta_4^{25}=0.8643$, $n^{25}{}_D=1.4032$. Visible region: $l=10$ cm. U.V. region: $l=5$ cm. Measurements on dextro form.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{8.9368}{\lambda^2-0.02225}$
5780.1	−2.714	− 28.66	− 28.66
5460.7	−3.192	− 32.37	− 32.38
4358.3	-5.25_7	− 53.2_9	− 53.2_9
4046.6	-6.21_0	− 62.9_7	− 63.1_6
3440	−4.58	− 92.9	− 93.0
3300	−5.08	$-103._0$	$-103._1$
3240	−5.33	$-108._1$	$-108._0$
3180	−5.58	$-113._2$	$-113._3$
3080	−6.08	$+123._3$	$-123._1$
2985	−6.58	$-133._4$	$-133._1$
2940	−6.83	$-138._5$	$-139._2$

TABLE VI. *Rotatory dispersion of levo-α-methyldodecylic acid in heptane.*

Constant of sample: $n^{25}{}_D=1.4403$. Visible region: Concentration 0.8489 M, $\delta_4^{25}=0.7240$, $l=20$ cm. U.V. region: Concentration 0.8573 M, $\delta_4^{25}=0.7244$, $l=10$ cm. Measurements on dextro form.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{8.6638}{\lambda^2-0.03446}$
6678.1	− 3.57_0	− 21.0_2	− 21.0_5
5875.6	− 4.733	− 27.87_7	− 27.87_9
5780.1	− 4.909	− 28.91_4	− 28.91_4
5460.7	− 5.580	− 32.86_6	− 32.85_1
4358.3	− 9.46_0	− 55.7_2	− 55.7_2
3890	− 6.40	− 74.6	− 74.1
3665	− 7.40	− 86.3	− 86.7
3510	− 8.40	− 98.0	− 97.6
3248	−10.40	$-121._3$	$-122._0$
3180	−10.90	$-127._1$	$-130._0$
3120	−11.40	$-133._0$	$-138._0$
2670	− 2.00 (1 cm)	−233	−235
2630	− 2.10 (1 cm)	−245	−249

TABLE VII. *Rotatory dispersion of levo-β-methylvaleric acid in heptane.*

Constant of sample: $n_D^{25}=1.4140$. Visible region: Concentration 0.8598 M, $\delta_4^{25}=0.7060$, $l=40$ cm. U.V. region: Concentration 0.8598 M for first 8 measurements, 0.8616 M for the others. $l=20$ cm for λ3820 to 3040, 10 cm for λ3210 to 2500, 5 cm for λ2495 to 2464, 1 cm for last two measurements.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{3.5876}{\lambda^2-0.01254}$	$[M]^{25}=-\frac{8.088}{\lambda^2-0.042}-\frac{11.68}{\lambda^2-0.034}$
6678.1	-2.84_5	− 8.27_2	− 8.27_8	− 8.33
5780.1	-3.837_5	-11.15_7	-11.15_7	−11.23
5460.7	-4.322_1	-12.56_6	-12.56_0	−12.64
4358.3	-6.95_5	−20.22	−20.22	−20.22
3820	−4.60	−26.7		−26.5
3660	−4.90	−28.5		−28.9
3600	−5.20	−30.2		−29.8
3500	−5.50	−32.0		−31.5
3420	−5.80	−33.7		−32.9
3350	−6.10	−35.5		−34.1
3040	−6.70	−39.0		−39.5
3210	−3.20	−37.1		−36.7
2690–3100	−3.30	−38.3		−38.1 −38.6
2720–3000	−3.40	−39.5		−39.2 −40.1
2850	−3.50	−40.6		−41.1

λ	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{8.088}{\lambda^2-0.042}-\frac{11.68}{\lambda^2-0.034}$
2650	−3.10	− 36.0	− 35.9
2615	−2.90	− 33.7	− 33.1
2605	−2.70	− 31.3	− 32.2
2575	−2.50	− 29.0	− 28.8
2568	−2.30	− 26.7	− 27.8
2550	−2.10	− 24.4	− 25.2
2535	−1.90	− 22.0	− 22.6
2525	−1.70	− 19.7	− 20.8
2500	−1.30	− 15.1	− 15.3
2495	−0.60	− 14	− 14.0
2478	−0.40	− 9.0	− 9.4
2464	−0.30	− 7.0	− 5.0
2395	+0.55	+ 64	+ 26
2300	+0.10 conc. 0.086 M	+120	+120

TABLE VIII. *Rotatory dispersion of levo-ethyl ester of β-methylvaleric acid without solvent.*

Constants of sample: $\delta_4^{25}=0.8644_3$, $n_D^{25}=1.4040$. Visible region: $l=10$ cm. U.V. region: $l=5$ cm, $l=1$ cm for last 3 measurements.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{3.7826}{\lambda^2-0.01911}$	$[M]^{25}=\frac{11.614}{\lambda^2-0.0420}-\frac{15.364}{\lambda^2-0.0373}$
				$+ 38.30_1$
				$- 49.89_4$
5875.6	− 6.947	-11.58_3	-11.59_9	$- 11.59_3$
				$+ 39.76_1$
				$- 51.76_6$
5780.1	− 7.193	-11.99_3	-12.00_8	$- 12.00_5$
				$+ 45.33_2$
				$- 58.88_9$
5460.7	− 8.129	-13.55_4	-13.55_4	$- 13.55_7$
				$+ 78.50_0$
				-100.65
4358.3	−13.28	−22.14	−22.14	− 22.15
				$+ 95.39_7$
				-121.51
4046.6	−15.66	−26.11	−26.15	− 26.11

λ	α^{75}	$[M]^{25}$	$[M]^{25}=\frac{11.614}{\lambda^2-0.0420}-\frac{15.364}{\lambda^2-0.0373}$
3775	− 9.20	−30.7	−30.5
3610	−10.20	−34.0	−33.7
3465	−11.20	−37.3	−36.9
3320	−12.20	−40.7	−40.5
3195	−13.20	−44.0	−43.9
2990	−15.15	−50.5	−49.9
2887	−16.15	−53.8	−52.8
2850	−16.40	−54.7	−53.7
2805	−16.65	−55.6	−55.7
2760	−16.90	−56.4	−55.4
2590	− 3.10	−51.7	−52.8
2558	− 2.95	−49.2	−50.5
2545	− 2.80	−46.7	−49.3

TABLE IX. *Rotatory dispersion of dextro-β-methylcaproic acid in heptane.*[18]

Constant of sample: $n_D^{25}=1.4220$. Visible region: Concentration 0.8678 *M*, $\delta_4^{25}=0.7090$, $l=100$ cm. U.V. region: Concentration 0.8556 *M*, $\delta_4^{25}=0.7086$, $l=10$ cm. Measurements on levo form.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{1.2580}{\lambda^2-0.02845}$
6678.1	2.62	3.02	3.01_3
5875.6	3.441	3.965	3.972
5780.1	3.572	4.116	4.116
5460.7	4.049	4.666	4.664
4358.3	6.76_0	7.79_0	7.79_0
4046.6	3.22 (40 cm)	9.28	9.30
3260	1.40	16.4	16.2
3050	1.70	19.9	19.5
2980	1.75	20.5	20.8
2765	2.30	26.9	26.2
2680	2.50	29.2	29.0
2610	2.70	31.5	31.7
2570	2.85	33.3	33.4
2390	0.45 (1 cm)	53	43.9

[18] The low value found for λ_0^2 and the absence of any appreciable curvature seem to indicate that the first two rotatory contributions have the same sign.

TABLE X. *Rotatory dispersion of dextro sodium salt of β-methylcaproic acid in water.*

Visible region: Concentration 0.7663 *M*, $\delta_4^{25}=1.024_5$, $l=40$ cm. U.V. region: Concentration 0.7663 *M*, $\delta_4^{25}=1.024_5$, $l=5$ cm. Measurements on levo form.

λ	5780.1	5460.7	4358.3	2730	2590	2500
α^{25}	0.810	0.916	1.51_0	0.60	0.70	0.80
$[M]^{25}$	2.92_4	3.30_8	5.45	$17._3$	$20._2$	$23._1$
$[M]^{25}=\frac{9.096}{\lambda^2-0.023}$	2.92_4	3.30_5	5.45	$17._6$	$20._6$	$23._0$

In fact, it is possible to express the experimental results almost within the limits of error, by a formula such as

$$[M]^{25}=\frac{0.286}{\lambda^2-0.042}+\frac{0.983}{\lambda^2-0.022}$$

in which λ_1^2 has the same value (0.042) found for the lower homologue.

This would be an important exception in the homologues of the propionic acid series. These results induced us to repeat the dispersion measurements on another preparation of this acid. Measurements on both samples agreed very well.

TABLE XI. *Rotatory dispersion of dextro ethyl ester of β-methylcaproic acid without solvent.*

Constants of sample: $\delta_4^{25}=0.8627_5$, $n_D^{25}=1.4100$. Visible region: $l=10$ cm. U.V. region: $l=5$ cm. Measurements on levo form.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{1.7008}{\lambda^2-0.05288}-\frac{1.6665}{\lambda^2-0.01951}$	λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{1.7008}{\lambda^2-0.05288}-\frac{1.6665}{\lambda^2-0.01951}$
5780.1	0.211	0.751	0.753	2935	3.70	26.3	26.1
5460.7	0.264_5	0.941	0.953	2910	4.00	28.4	27.9
4358.3	0.74_0	2.63	2.63	2854	4.60	32.7	32.6
4046.6	1.06_5	3.78_7	3.78_7	2835	4.90	34.8	34.5
3400	1.40	9.95	9.77	2790	5.60	39.8	39.6
3300	1.60	11.3	11.7	2770	6.00	42.7	42.2
3240	1.80	12.8	13.1	2750	6.40	45.5	45.1
3210	2.00	14.2	14.0	2710	7.20	51.2	51.8
3155	2.20	15.6	15.6	2700	7.60	54.0	53.7
3092	2.50	17.8	17.9	2667	8.60	61.2	60.9
3050	2.80	20.0	19.7	2630	10.10	71.8	70.8
3010	3.10	22.1	21.7	2605	11.10	78.9	79.0

TABLE XII. *Rotatory dispersion of dextro-β-methylheptylic acid in heptane.*

Constant of sample: $n_D^{25}=1.4243$. Visible region: Concentration 0.8481 M, $\delta_4^{25}=0.7105$, $l=40$ cm. U.V. region: Concentration 0.8535 M, $\delta_4^{25}=0.7109$, $l=10$ cm. Measurements on levo form.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{1.9022}{\lambda^2-0.04665}$	$[M]^{25}=\frac{1.996}{\lambda^2-0.04916}$	λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{1.996}{\lambda^2-0.04916}$
5875.6	0.814_5	6.35_8	6.37_1		3150	1.30	$40._3$	$39._9$
5780.1	0.848	6.61_8	6.61_8		3095	1.40	$43._4$	$42._8$
5460.7	0.972	7.58_7	7.56_3		3035	1.50	$46._5$	$46._5$
4358.3	1.70_0	13.2_7	13.2_7		3000	1.60	$49._6$	$48._9$
3660	0.70	$21._7$		$23._5$	2920	1.80	$55._8$	$55._3$
3590	0.80	$24._8$		$25._0$	2860	2.00	$62._0$	$61._2$
3430	0.90	$27._9$		$29._1$	2810	2.20	$68._2$	$67._0$
3370	1.00	$31._0$		$31._0$	2765	2.40	$74._4$	$73._1$
3280	1.10	$34._1$		$34._2$	2680	2.80	$86._9$	$88._1$
3215	1.20	$37._2$		$36._8$	2540	4.20	$130._0$	$130._0$

TABLE XIII. *Rotatory dispersion of dextro-β-methylcaprylic acid in heptane.*

Constants of sample: $\delta_4^{25}=0.8984_5$, $n_D^{25}=1.4290$. Visible region: Concentration 0.8629 M, $\delta_4^{25}=0.7138$, $l=40$ cm. U.V. region: Concentration 0.8629 M, $\delta_4^{25}=0.7138$, $l=5$ cm. Measurements on levo form.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{2.5458}{\lambda^2-0.04554}$	$[M]^{25}=\frac{2.438}{\lambda^2-0.04836}$	λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{2.438}{\lambda^2-0.04836}$
5875.6	2.830	8.492	8.495		2850	3.10	74.4	74.2
5780.1	2.940	8.822	8.822		2765	3.60	86.4	86.8
5460.7	3.358	10.07_6	10.07_6		2643	4.60	110	113
4358.3	5.875	17.62_9	17.62_9		2597	5.35	128	128
4046.6	7.180	21.54_5	21.53_7		2550	6.10	146	146
3510	1.35	32.4		32.6	2538	6.35	152	152
3330	1.60	38.4		39.0	2524	6.60	158	159
3110	2.10	50.4		50.4	2515	6.85	164	164
2957	2.60	62.4		62.4	2505	7.10	170	169
					2485	7.60	182	182

TABLE XIV. *Rotatory dispersion of dextro ethyl ester of β-methylcaprylic acid without solvent.*

Constants of sample: $\delta_4^{25}=0.8595$, $n_D^{25}=1.4189$. Visible region: $l=10$ cm. U.V. region: $l=5$ cm. Measurements on levo form.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{1.2066}{\lambda^2-0.05523}$	$[M]^{25}=\frac{1.3143}{\lambda^2-0.0529}-\frac{0.1087}{\lambda^2-0.019}$	λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{1.3143}{\lambda^2-0.0529}-\frac{0.1087}{\lambda^2-0.019}$
5780.1	1.928_5	4.327	4.327	4.329	2755	12.15	54.5	55.2
5460.7	2.216	4.972	4.966	4.969	2725	13.15	59.0	59.6
4358.3	3.99_2	8.956	8.956	8.954	2697	14.15	63.5	64.2
4046.6	4.95_0	11.106	11.119	11.106	2678	15.15	68.0	67.8
3256	5.15	23.1		23.5	2652	16.15	72.5	73.3
3130	6.15	27.6		27.8	2635	17.15	77.0	77.4
3030	7.15	32.1		32.3	2620	18.15	81.4	81.3
2948	8.15	36.6		37.0	2603	19.15	85.9	86.2
2885	9.15	41.1		41.6	2590	20.15	90.4	90.4
2832	10.15	45.5		46.4	2561	4.65 (1 cm)	104	105
2792	11.15	50.0		50.6				

TABLE XV. *Rotatory dispersion of levo-γ-methylcaproic acid in heptane.*

Constant of sample: $n_D^{25}=1.4213$. Visible region: Concentration 0.8312 *M*, $\delta_4^{25}=0.7080$, $l=40$ cm. U.V. region: Concentration 0.8520 *M*, $\delta_4^{25}=0.7087$, $l=20$ cm and 10 cm.

λ	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{4.593}{\lambda^2-0.02172}$	$[M]^{25}=\frac{3.825}{\lambda^2-0.042}-\frac{8.395}{\lambda^2-0.032}$
5892.6	-1.213_5	−14.10	− 14.11	−14.10
5780.1	-1.265_5	−14.70	− 14.70	−14.70
5460.7	-1.429_5	−16.61	− 16.61	−16.61
4358.3	-2.35_0	−27.30	− 27.30	−27.30
3480	−2.00 (20 cm)	−45.3	− 46.2	−45.9
3220	−1.20 (10 cm)	−54.4	− 56.9	−55.1
3095	−1.30 (10 cm)	−58.9	− 62.0	−60.5
2900	−3.00 (20 cm)	−68.0	− 72.3	−70.3
2830	−3.20 (20 cm)	−72.5	− 80.3	−74.2
2730	−3.40 (20 cm)	−77.1	− 87.0	−79.8
2530	−1.95 (10 cm)	−88.5	−108.6	−88.5

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Exchange Reactions of Protium and Deuterium [1]

Investigations concerning the chemical nature of deuterium have been in progress for some time. The adequate analysis of small amounts of deuterium-rich hydrogen has proved of considerable difficulty, but the interest in the properties of deuterium justifies this preliminary notice.

A sample of water containing one percent deuterium[2] was circulated with ordinary hydrogen by means of a mercury jet pump through a quartz tube at 800°C for several days. The hydrogen was then freed from the original water by liquid air traps and phosphorus pentoxide. Photographs of the atomic discharge of this hydrogen and of ordinary hydrogen were made on the 21-foot grating. The discharge tube was swept out repeatedly with air and then run with several fresh samples of ordinary hydrogen. The deuterium line $H^2\beta$ was about one-fourth the intensity of the fourth order ghost from the protium $H^1\beta$. The discharge tube was then run with several samples of the prepared hydrogen. The deuterium $H^2\beta$ of this hydrogen was of greater intensity than the fourth order ghost from $H^1\beta$. No effort was made to estimate the concentration of deuterium as experiments are in progress with more concentrated samples of water and better analytical methods. These experiments deal with the nature of the exchange reported here as well as the atomic metathesis of this and other suitable reactions.

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[1] These names have been proposed for the ordinary hydrogen atom and the isotope by Urey, Brickwedde and Murphy, J. Chem. Phys. **1**, 512 (1933).

[2] This was kindly supplied by Professor H. C. Urey.